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THE CONDENSATION OF ALDEHYDES WITH AMIDES.

Part I. The Condensation of Salicylaldehyde.

By Kantilal C. Pandya and Tejpal Singh Sodhi.
(From the Department of Chemistry, St. John's College, Agra.)

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The condensations of aldehydes with acid amides have been studied by a very large number of workers and the literature is extensive. Often the condensation is brought about by merely heating the aldehyde with the amide alone: in other cases condensing agents of several kinds have been used, such as, hydrogen chloride, potassium hydroxide, potassium carbonate, diethylamine, triethylamine, sulphuric acid dilute, anhydrous sodium acetate with, or without, acetic anhydride. Frequently, the condensation has been carried out without a solvent. Reich[1] alone has used pyridine, but he has employed 1 to 1·5 mols. of pyridine for every mol. of the aldehyde and has generally carried out the condensations in sealed tubes by heating at high temperatures, about 180° C., and for 12 hours or so.

The observation made in this Laboratory, of the rôle of organic bases, and particularly of pyridine, as catalysts in promoting condensations of a different type, *viz.*, of the aldehydes with malonic acid, and yielding an exceedingly simple and successful method, of synthesising $\alpha\beta$-unsaturated acids,[2] prompted the inquiry whether the aldehyde-amide condensations also would be susceptible to similar catalytic influences. The perusal of the condensations of salicylaldehyde, which have all been conducted so far by means of heating with anhydrous sodium acetate only, and the fact that this was the aldehyde the study of whose condensation with malonic acid first led to the observation of the catalytic effect of pyridine,[3] made the choice of salicylaldehyde, as the first aldehyde to be studied in this series, altogether inevitable.

In order to make comparisons fair in respect of procedure and of yields, the earlier condensations have been repeated, *viz.*, the condensations of the aldehyde with benzamide, formamide and acetamide, achieved by heating with anhydrous sodium acetate by Cebrian[4] first, and later on by Titherley and Marples.[5] The latter authors have, however, confined themselves to only the first condensation, namely with benzamide, but have identified

the condensation-product correctly as salicylidene-benzamide. Our observations entirely confirm this structure in the case of this product as well as in the cases of the products obtained from other amides, which were identical in properties with those obtained by Cebrian with the same method. The condensations of salicylaldehyde were then repeated by the new method, namely, by heating in the presence of traces of pyridine, piperidine and lutidine respectively. The products were the same as before, namely, salicylidene-benzamide, salicylidene-formamide and salicylidene-acetamide. Propionamide and phenylacetamide were also tried for the first time, and they fell in a line with the other amides, giving salicylidene-propionamide and salicylidene-phenylacetamide, which are thus prepared for the first time.

The organic bases employed are thus as effective as sodium acetate: nay, they are even more, in several distinct ways. It was possible to carry out the reaction at a lower temperature than 160–70° C., so often employed with sodium acetate, resinification was thus reduced or altogether avoided, and the alkylidene-amides were uniformly cleaner, purer and in larger yields (*vide* tables). Moreover, the organic base was a true catalyst, as in every case condensation would occur even when the aldehyde and the amide were heated alone without the base or without any condensing reagent, but proceeded to a lesser extent during the same period of heating, or required much longer heating to give comparably good yields, as were obtained in the presence of a trace of the base.

With respect to the course of the reaction, Titherley and Marples[5] suggest three different possibilities:

a. $-CHO + H_2NCOR \rightarrow -CH(OH).NHCO\cdot R$

b. $-CHO + H_2NCOR \rightarrow -CH=NCO\cdot R + H_2O$

c. $-CHO + H_2NCOR \rightarrow -HC\begin{matrix}NHCO\cdot R\\NHCO\cdot R\end{matrix} + H_2O$

where R is the alkyl or aryl radical in the acid amide. *a* is the simple aldol condensation, giving aldol-like products (Einhorn and others[6]). *b* is the straightforward condensation, eliminating water and giving, as in the present case, salicylidene-amides, or similar products. The *c* requires two molecules of the amide for every one of the aldehyde and gives the -bisamide, like benzylidene-bisbenzamide, and so on.[7,1] Similar products have also been obtained in our Laboratory, *viz.*, cinnamylidene-bisamides, by Mehra.[8] (The last paper will soon be published.)

The product in any condensation may, therefore, be any one of the above three types, or may be even a mixture of two or more. In the present case the structure is, beyond doubt, the one obtained exclusively by *b*.

Apart from the arguments given by Titherley and Marples,[5] a number of observations confirm the conclusion. The evolution of copious water-vapours rules out *a*. All our products instantly decolorise Baeyer's reagent in the cold, indicating unsaturation, and the reaction takes place between one molecule of the aldehyde and one of the amide, which rule out *c*. Further confirmation is given by analysis.

The salicylidene-amides are, at the end of the reaction in the flask, yellow or brown, transparent and often hard, looking very much like " organic glass ". Their behaviour with solvents is peculiar, and it was difficult or impossible to crystallise them from any solvent. They gave a pink coloration with concentrated sulphuric acid, as noted by earlier workers.

Titherley and Marples[5] have separated the crude salicylidene-benzamide obtained by them into two isomers, the α- and β-forms, as they are called. This observation is confirmed, and the two forms have been obtained as described, not only from the condensation carried out in the presence of anhydrous sodium acetate, but also from the products obtained from the condensations carried out in the presence of a trace of pyridine or of piperidine. The α-form alone was, however, obtained when the condensation took place in the presence of a trace of lutidine as well as when it took place without the presence of any reagent whatever.

Salicylidene-formamide was more easily recrystallised than the others. It was also obtained in quantitative yields when lutidine was employed and also gave the sharpest melting-point in the series (98° C.), and yet the crude product, left in a sample-tube, was found, after a few months, to have changed into a dark red resin.

EXPERIMENTAL.

Condensation of salicylaldehyde with benzamide.—

(i) *In the presence of anhydrous sodium acetate.*—Salicylaldehyde 10 g., benzamide 10 g. and sodium acetate anhydrous 6 g. (1 : 1 : 1 mol.) were mixed (Cebrian[4]) in a 250 c.c. open flask and heated on an oil-bath at 140° C. for five hours. At 110° C. copious vapours of steam came out and at 120–25° C. the reacting mass became one clear liquid. No condenser was used. After five hours' heating, the flask was allowed to be cool and was filled up with 200 c.c. of water. The next morning the solid was taken out, crushed in a mortar with plenty of cold water, dried and weighed. Yield 14·2 g., or 77% of theory. Its properties were as described by Titherley and Marples[5] and it could be separated by means of acetone into the soluble or the α-form

and the insoluble or β-form. On heating, the α-form did not melt but started to decompose at 195–96° C. (Ti. and Mar. give 190°). The β-form started to decompose at 198–205° C. (Ti. and Mar. give 200°). In amount the α-form was about twice that of the β-. A mixed melting-point showed no change, the decomposition starting at 195–96°.

(ii) *With a trace of pyridine.*—Salicylaldehyde 3 g., benzamide 3 g. and pyridine 0·285 g. (1 : 1 : 0·15 mol.) were heated in the same way in an open flask without a condenser, at 130–40° C., for three to four hours, and the flask was left to cool by itself overnight. Next morning the product was taken out with cold water, washed and dried. The dried product was not brown as in the preceding experiment but was yellow and weighed after purification 5·3 g., the yield being thus 96·4% of theory. It was identical with the product obtained by Cebrian's method and could be resolved in the same way into the α- and the β-form.

(iii) *With a trace of piperidine.*—The experiment (ii) was repeated with 0·315 g. of piperidine instead of pyridine. The product and the yield were exactly the same, 5·3 g. or 96·4%.

(iv) *With a trace of lutidine.*—With 0·390 g. of lutidine, the yield, though still very good, was a little less, namely 4·4 g. or 80%. The product was brownish, dissolved completely in acetone and was thus the α-form, without any admixture of the β-.

(v) *Without any reagent.*—Under the same conditions, but without any base or without sodium acetate, the product again was the α-form alone. The yield on five hours' heating was 5 g. or 91% of theory, and was thus higher than was obtained by Cebrian's method above.

The acetone-soluble salicylidene-benzamide was found to contain N = 5·9%. Calc. N = 6·2 %.

TABLE I.

Heated with	Proportions	Time	Temperature	Product	
				Wt. %	Yield Colour
Sodium acetate anhydrous	1 : 1 : 1 mol.	5 hrs.	140° C.	77	Brown ; pale yellow (pure)
Pyridine ..	1 : 1 : 0·15 ,,	3–4 ,,	130–40°	96·4	Yellow
Piperidine ..	,, ,,	,, ,,	,,	96·4	,,
Lutidine ..	,, ,,	,, ,,	,,	80·0	Brown, α- only
Alone ..	1 : 1 : 0·0 ,,	5 ,,	,,	91·0	Yellow, α- only

Condensation with formamide.—

(i) *With sodium acetate anhydrous.*—Salicylaldehyde 12 g., formamide 4 g. and anhydrous sodium acetate 6 g. were heated on the water-bath (according to Cebrian[4]) for five hours in an open flask; water vapour soon came off and the whole mass turned liquid. Treated as before, it gave a brown powder, weighing 5 g. (yield = 34 %), and melting at 90–1° C. After recrystallization from alcohol, the melting point rose to 98° C. (Cebrian gives 98°). It was lemon-yellow in colour, and resembled in properties, etc., the salicylidene-formamide described by previous workers.

(ii) *With a trace of pyridine.*—Salicylaldehyde 3 g., formamide 1 g. and pyridine 0·285 g. (1 : 1 : 0·15 mol.) were heated on a water-bath for eight hours, left overnight and the salicylidene-formamide extracted as usual. Yield 3·1 g. or 87% of theory. The heating had to be longer than usual, otherwise a viscous mass was formed and the yield was diminished.

(iii) *With a trace of piperidine.*—0·315 g. of piperidine was used instead of pyridine. Even after 8 hours' heating, the product was a dark brown viscous mass, which gave only 1·3 g. or 36·5% yield. The condensation was repeated with twice the molecular proportions of formamide, in order to replace the formamide lost on heating, but the result was not affected.

(iv) *With a trace of lutidine.*—With 0·390 g. of lutidine as the base, and with 8–10 hours' heating, the yield improved to 3·5 g. or 100%.

(v) *Without any reagent.*—Several experiments were made with changes in the period of heating. With 18 hours' heating the yield became 2·8 g. or about 81% of theory.

On analysis salicylidene-formamide gave N = 9·5 %. Calc. N = 9·5%.

TABLE II.

With	Proportions Molar	Temp.	Time of heating	Yield %	Colour
Sodium acetate anhydrous ..	1 : 1 : 1	100°	5 hours	34	Brown
Pyridine ..	1 : 1 : 0·15	,,	8 hours	87	Lemon-yellow
Piperidine ..	,,	,,	,,	36	Brown
Piperidine ..	1 : 2 : 0·15	,,	,,	36	,,
Lutidine ..	1 : 1 : 0·15	,,	8–10 hours	100	Yellow
Nothing	1 : 1 : 0·0	,,	18 hours	81	,,

Condensation of salicylaldehyde with acetamide.—

(i) *With sodium acetate anhydrous.*—Cebrian's experiment was repeated. 10 g. of the aldehyde, 5 g. acetamide and 6 g. anhydrous sodium acetate, heated at 140° C. for 4 hours, gave with the usual treatment 12·4 g. of salicylidene-acetamide (yield = 90 %). It was brown and amorphous, and after repeated purifications became lighter in colour ; it did not melt but decomposed between 160° and 170° C. (Cebrian says ' turns brown and decomposes at 150° C.').

(ii) *With a trace of pyridine.*—Salicylaldehyde 3 g., acetamide 1·5 g. and pyridine 0·19 g., were heated for four hours at 130–40° C. The salicylidene-acetamide obtained weighed 3·8 g. (yield = 98 %).

(iii) *With a trace of piperidine.*—The same amounts of the aldehyde and the amide with 0·21 g. of piperidine, gave 3·5 g. or 93% yield.

(iv) *With a trace of lutidine.*—With 0·260 g. of lutidine and heating for 4–5 hours at 130–40° C., the yield was 3·5 g. or 98%.

(v) *Without any reagent.*—Heating alone at 140° C. for 5 hours gave an yield of 3·5 g. (93%).

Salicylidene-acetamide was found to contain N = 8·98%. Calc. N = 8·5 %.

TABLE III.

With	Proportions Molar	Temp.	Time	Yield %	Colour
Sodium acetate anhydrous ..	1 : 1 : 1	140°	4 hours	91	Yellow-brown
Pyridine ..	1 : 1 : 0·10	130–40°	,,	98	Bright yellow
Piperidine ..	,,	,,	,,	93	Dirty ,,
Lutidine ..	,,	,,	4–5 ,,	98	Yellow
No reagent ..	1 : 1 : 0·0	140°	5 hours	93	Brownish yellow

Condensation of salicylaldehyde with propionamide.—

(i) *With sodium acetate anhydrous.*—3 g. salicylaldehyde, 1·8 g. propionamide and 3 g. sodium acetate anhydrous were heated at 140° C. for 4 hours. Salicylidene-propionamide came out as a brown yellow amorphous powder, weighing 4·1 g., but containing some resinous matter, which was removed by means of pyridine, in which it did not dissolve. The filtered pyridine solution gave a bright yellow solid which was sparingly soluble in hot alcohol, but insoluble in most of the ordinary solvents. It resembled

the other products described above in almost all respects. The repeatedly purified solid did not melt but started to decompose at 190–95° C. After purification, the yield was 3·2 g. or 73%.

(ii) *With a trace of pyridine.*—Salicylaldehyde 1·2 g., propionamide. 0·7 g. and pyridine 0·12 g. on heating at 130–40° C. for 3–4 hours gave a bright yellow product, which was identical, weighing 1·5 g. = 88·2% of theory.

(iii) *With a trace of piperidine.*—With 0·13 g. of piperidine the same amounts of the aldehyde and the amide gave, under the same conditions, 1·3 g. or 76·4 % yield.

(iv) *With no reagent.*—Under the same conditions, the yield was 1·2 g. or 70·5%.

The salicylidene-propionamide gave on analysis :—C = 67·48 %, H = 6·21% and N = 7·6%. Calc. C = 67·7%, H = 6·2% and N = 7·9%.

TABLE IV.

With	Proportions Molar	Temp.	Time	Yield %	Colour
Sodium acetate anhydrous ..	1 : 1 : 1	140°	4 hours	73	Yellow
Pyridine ..	1 : 1 : 0·15	130–40°	3–4 hours	88·2	Bright yellow
Piperidine ..	,,	,,	,,	76·4	,,
No reagent ..	1 : 1 : 0·0	130–40°	,,	70·4	,,

Condensation of salicylaldehyde with phenylacetamide.—

Phenylacetamide was prepared (m.p. 154–55° C.) in a good yield and in a very pure condition by treating phenylacetic acid with thionyl chloride and then treating the acid chloride in the usual way with strong ammonia.

(i) *With anhydrous sodium acetate.*—Salicylaldehyde 2·4 g., phenylacetamide 2·7 g. and sodium acetate anhydrous 1·6 g. were heated for 4 hours at 140° C. and the salicylidene-phenylacetamide mixed up with some resin was taken out as usual. On purification the yield was found to be about 65 %.

(ii) *With a trace of pyridine.*—The same amounts of the aldehyde and the amide were heated with 0·285 g. of pyridine at 140°. As usual the water-vapours were given off and the whole mass became a liquid, which soon began to set again to a solid, indicating a quicker reaction. After 2–3 hours' heating, salicylidene-phenylacetamide was taken out as a lemon-yellow

powder. It resembled in properties the other members described above. After purification it melted at 110–14° C. The yield was 4·1 g. or 8·57%.

(iii) *With a trace of piperidine.*—0·315 g. of piperidine was used in place of pyridine, and the yield under the same conditions was 3·5 g. or 73%.

(iv) *With a trace of lutidine.*—With 0·390 g. of lutidine, the yield came up to 3·1 g. or about 65% after 5 hours' heating.

(v) *With no reagent.*—Heated alone for 4 hours, the two gave an yield of 2·8 g. or 58%.

The salicylidene-phenylacetamide gave on analysis:—Found: C = 75·23 %, H = 5·9 % and N = 5·8 %. Calc. C = 75·3 %, H = 5·3 % and N = 5·8 %.

TABLE V.

With	Proportions Molar	Time	Yield %	Colour
Sodium acetate anhydrous ..	1 : 1 : 1	4 hours	65	Brown
Pyridine	1 : 1 : 0·15	2–3 hours	85·7	Lemon yellow
Piperidine ..	,,	,,	73	,,
Lutidine ..	,,	4–5 hours	65	,,
No reagent ..	1 : 1 : 0·0	4 hours	58	Brownish yellow

The heating was throughout at 140° C.

SUMMARY.

The condensation of salicylaldehyde with five different amides has been studied, using anhydrous sodium acetate, a trace of an organic base as a catalyst or using no reagent whatsoever.

A comparison is made of the yields obtained, and it is found that the catalytic influence of a base promotes the reaction better, and gives a purer product than was obtained by the usual sodium acetate method.

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CONDENSATION OF MALONANILIC ACID WITH AROMATIC ALDEHYDES.

By Rup Kishore Mehra and Kantilal C. Pandya.
(From the Department of Chemistry, St. John's College, Agra.)

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Ahluwalia, Haq and Ray[1] have carried out condensations of certain aromatic aldehydes with malonanilic acid and its derivatives in pyridine-piperidine solution. The method is essentially the widely-used method of Robinson and Shinoda.[2] The aldehyde and the acid are in molecular proportions, while about 3·5 mols. of pyridine are taken with a few drops of piperidine.

In studying the condensations of aromatic aldehydes with malonic acid, one of the authors (P.) had occasions to make a comparative study of this method with that of using a trace only of a single base like pyridine or piperidine.[3] We have, therefore, extended our study to the condensation, by both the methods, of malonanilic acid with several aromatic aldehydes. We find that as a rule the condensations take place equally well when a trace of a single base is used ; in this case we have used only pyridine and piperidine. Not only so, but the condensation-products are formed in greater yields by our method.

Three of the aldehydes selected by us are those which Ahluwalia, Haq and Ray have also used, *viz.*, piperonal, salicylaldehyde and *o*-nitrobenzaldehyde. In addition, five more aldehydes have been condensed with malonanilic acid, *viz.*, benzaldehyde, *m*-hydroxybenzaldehyde, *p*-hydroxybenzaldehyde, *m*-nitrobenzaldehyde and *p*-nitrobenzaldehyde, all of which condense readily with malonanilic acid by both the methods and give decidedly higher yields with the trace-method. Excepting in the case of the last two aldehydes, Ahluwalia, Haq and Ray's method also has been applied to each case, in order to make a fair comparison and in order also to obtain figures of the yields not available in the paper of these authors. Even when the figures are available there, the yields and the products obtained by us are not always identical with those reported by these authors.

These differences are indicated in the experimental account. The main difference lies in the nature of the products obtained in the condensation of *o*-nitrobenzaldehyde. Ahluwalia, Haq and Ray obtain *o*-nitrobenzylidenemalonanilic acid "in good yield," with "very little of the decarboxylated

product in the reaction at 100°." Our general experience of a higher temperature, in this case 100° in place of 50–60° originally employed, would lead us to expect greater decarboxylation, and in this particular case, when the experiment was repeated, we got only the decarboxylated anilide and no acid. The anilide happened to be in two forms, one white and the other pale yellow, which could be separated and which gave each different melting-points, the white melting at 172° and the yellow at 188–90°. As the expected acid has also the same melting-point, 172°, as one of these, [(1), p. 2061], it was at first taken to be the *o*-nitrobenzylidenemalonanilic acid. But it did not react at all with sodium carbonate solution, and the determinations of its nitrogen, carbon and hydrogen contents clearly established it as the *o*-nitrocinnamanilide. The yellow substance also behaved exactly alike with sodium carbonate solution and gave almost identical figures for the carbon, hydrogen and the nitrogen contents. There is thus no doubt that none of them is the acid, and that both have the same composition of the anilide. During the time these points were settled, it was observed that the white was very unstable to light and gradually, though quickly in the beginning, changed over into the pale yellow. Starting with the white, m.p. 172°, in diffused light, a distinct colour had developed and the melting-point was lowered to 161° in one week, to 159° in ten days and remained there for two weeks more. During this period, the mixed anilide could at any time be resolved, by means of suitable solvents, into the white and the yellow.

It is hoped to study this more closely with a view to understand clearly the structure-relationship of the two and to ascertain whether the change is isomerisation or polymerisation.

It may be noted that the yields obtained with the *m*- and the *p*-, hydroxy-and-nitro-benzaldehydes were greater than those obtained with the corresponding *o*-isomers.

p-Tolylaldehyde has also been condensed and gave about 71% yield of the cinnamanilide. It has, however, not been reported under the experimental, as sufficient sample was not available for purification and full analysis.

EXPERIMENTAL.

Malonanilic acid was prepared according to the method of Chattaway and Olmsted[4] as modified by Ahluwalia, Haq and Ray.[1]

Condensation of malonanilic acid with piperonal.—

(*i*) *With pyridine-piperidine mixture.*—Ahluwalia, Haq and Ray's experiment was exactly repeated. We obtained only piperonylidenemalonanilic acid (1 g., yield = 32%), m.p. 202–03°, pale yellow needles. Ray

and co-workers report only 0·5 g. of this acid, but they obtained 1·3 g. of 3 : 4-methylenedioxycinnamanilide, which was not obtained by us. The non-acid fraction which we obtained was a brown oil, which solidified on keeping in a freezing mixture and was the unchanged piperonal (0·5 g.).

The same experiment was repeated in two different ways. In the one case, the reactants were in the same proportions but they were heated to a slightly higher temperature, 60–70°, and for 2 hours instead of one : the acid came out in the same amount, 1 g., but 0·1 g. of the cinnamanilide was also obtained (yield = 3·7%), m.p. 157°.

In the other case, the proportions of the two bases were changed, and 1·5 g. piperonal, 1·8 g. malonanilic acid, 3 c.c. of pyridine (instead of 4) and 2 drops of piperidine (instead of 4) were heated at 50–60° for one hour. The usual treatment gave 0·2 g. of the anilide (yield = 7·4%) and 1·0 g. of the acid.

(*ii*) *With a trace of one base only.*—The same amounts of the aldehyde and the acid were now taken with a trace of pyridine, the three being in 1 : 1 : 0·15 mol. proportions. The mixture was heated for five hours at 55–60°, and then one hour more at 60–65°. Some piperonal was still recovered unchanged (about 0·2 g.), no cinnamanilide was formed, and the piperonylidenemalonanilic acid was obtained, 1·1 g. (yield = 41%).

In the next experiment, the temperature was raised : the same quantities of the two were heated with piperidine on the water-bath for one hour only. The non-acid portion was wholly piperonal, about 0·7 g. and the acid was also about 0·7 g. Calculating on the 1·5 g. of piperonal taken, the yield would be about 26% only, but calculating on the piperonal actually used up, the yield would be about twice as much, or about 50%.

In the next two experiments, the same amounts of the aldehyde and of the acid were set up on the water-bath with 0·15 mol. of pyridine and of piperidine respectively. The heating was continued for four hours. The effect of this longer heating was to increase the yield : the pyridine-containing flask gave only 0·2 g. of the acid (yield 6·5%) and 1·2 g. of the decarboxylated anilide (yield = 45 %), and the piperidine-containing mixture gave 0·1 g. of the acid and 1·5 g. of the cinnamanilide (yield = 3·7 % and 56·2%, *i.e.*, total 60 % nearly). Some piperonal was still recovered unchanged. Ahluwalia, Haq and Ray found this anilide—" when kept or exposed to light, undergoes a change, possibly partial transformation into the geometric isimeride or an allo-form, which affects its m.p." We have been unable to confirm this, as a crude specimen, kept in an ordinary specimen-tube, examined after several months, retained its melting-point.

It is probable that the admixture of the unused piperonal is responsible for this reported change in the melting-point.

Condensation with salicylaldehyde.—

(*i*) *With pyridine-piperidine mixture.*—A., H. and R.'s experiment was repeated and 0·5 g. of yellow needles of coumarin-3-carboxyanilide was obtained, m.p. 247°. A., H. and R. do not state their yield : our yield was 18·9 % only.

The same experiment was repeated, but the mixture was heated, not on a water-bath but in an oil-bath at 100–04° for 4 hours, instead of one hour only. The yield increased to 0·8 g. or to 30·2 %.

(*ii*) *With only one base.*—The same amounts of the malonanilic acid and salicylaldehyde were heated with only 0·15 mol. of pyridine, at 100–104° for four hours. The yield was the same, *viz.*, 0·8 g. Repeating with the same but at a higher temperature still, 110–12°, the yield did not improve and remained stationary.

With piperidine, however (1 : 1 : 0·15 mol.), at 100–04° for four hours, the yield increased to 1·0 g., *i.e.*, to 37·8 %.

Condensation with *m*-hydroxybenzaldehyde.—

(*i*) *With pyridine-piperidine mixture.*—Malonanilic acid 1·8 g., *m*-hydroxybenzaldehyde 1·3 g. and a mixture of 3 c.c. of pyridine and 2 drops of piperidine were heated on the water-bath for one hour. On working up the product *m*-hydroxycinnamanilide was obtained, which recrystallised from aqueous alcohol, came out in brown silky needles, melting at 155–56°. Yield 1·6 g. or about 67 %.

(*ii*) *With any one base.*—The same amounts of the acid and of the aldehyde with a trace of pyridine were heated on the water-bath for five hours. The orange-coloured solid mass was dissolved in 10% aqueous sodium hydroxide, and dilute hydrochloric acid was added to precipitate the anilide. It was purified as before : yield 1·8 g. or 75·5 %.

The same experiment was repeated with a trace of piperidine and gave under the same conditions 1·9 g. or 79·6 % of the anilide.

The *m*-hydroxycinnamanilide gave a green colour with ferric chloride solution and gave a green fluorescence in NaOH solution. (Found : N = 5·7, 5·9 % ; C = 75·3 % ; H = 5·6 %. $C_{15}H_{13}O_2N$ requires N = 5·8 % ; C = 75·3 % ; H = 5·4 %.)

Condensation with *p*-hydroxybenzaldehyde.—

(*i*) *With pyridine-piperidine mixture.*—By repeating the above experiment with the *p*-aldehyde, 1·5 g. (62·7 %) of the *p*-hydroxycinnamanilide,

m.p. 208°, was obtained as pale yellow needles from dilute alcohol. It also gave a green colour with alcoholic ferric chloride.

(*ii*) *With a trace of one base.*—With pyridine and piperidine respectively in traces, on the water-bath for five hours, the yields were respectively 1·8 g. and 1·9 g., *i.e.*, 75·3 % and 79·6 %. (Found : N = 6·2, 5·87 % ; C = 75·4 % ; H = 5·39 %. $C_{15}H_{13}O_2N$ requires N = 5·8 % ; C = 75·3 % ; H = 5·4 %.)

Condensation with benzaldehyde.—

(*i*) *With pyridine-piperidine mixture.*—1·8 g. malonanilic acid, 1·1 g. benzaldehyde, 3 c.c. pyridine, and 2 drops of piperidine, heated on the water-bath for one hour, and worked up in the usual way, gave 1·8 g. cinnamanilide (80·7 %), in small silky white needles, m.p. 149–50°.

(*ii*) *With a trace of one base—i.e.*, with 0·15 mol. of pyridine and of piperidine respectively, on the water-bath with 4 hours' heating, the yields were 1·9 g. and 2 g. (= 85·2% and about 89·7 %).

On analysis cinnamanilide gave : N = 6·4, 6·3 % ; C = 80·99 % ; H = 6·2 %. $C_{15}H_{13}ON$ requires N = 6·28 % ; C = 80·7 % ; H = 5·8 %.

Condensation with *o*-nitrobenzaldehyde.—

(*i*) *With pyridine-piperidine mixture.*—On heating on the water-bath for one hour a mixture of 1·8 g. malonanilic acid, 1·5 g. *o*-nitrobenzaldehyde, 3 c.c. pyridine and 2 drops of piperidine (according to A., H. and R.'s method) and treating as usual, a pale yellow solid separated, which did not dissolve in sodium carbonate solution and which was later on separable (by repeated fractional crystallisations, with alcohol, acetone and benzene respectively), into two substances, one pale yellow, melting at 190°, and the other white, melting at 172°. The sodium carbonate extract on acidification gave nothing, indicating that no *o*-nitrobenzylidenemalonanilic acid was formed (contrast A., H. and R.). Both came out as small needles, the white was slightly more soluble in alcohol, while the yellow was slightly more soluble in benzene. The white was very unstable in ordinary light and gradually assumed a pale yellow tint and changed in melting-point. An observation of several weeks showed that this photochemical change continued for a long time though there was no evidence of a complete transformation of all the white into the yellow. Analysis showed that both had the same percentage composition, *viz.*, that of the anilide. (The white gave : C = 67·63, 67·20 % ; H = 4·72, 4·52 % ; N = 10·4, 10·62 % ; $C_{15}H_{12}O_3N_2$ requires C = 67·15 % ; H = 4·47 % ; N = 10·45 %. The yellow gave : C = 67·23 % ; H = 4·53 % ; N = 10·37, 10·29 % ; which also conform to the requirements of the same

formula.) The total yield was 1·1 g. which, assuming that the two forms were isomeric, would give 41 %. (A., H. and R. do not state the yield of their "acid", though they say it was "good," and the decarboxylated product was "very little".)

The same experiment was repeated with the difference that the heating was conducted at 100–04° for one hour. On cooling, as no solid was observable, the heating was continued for two more hours, and then finished by ten minutes' heating on a wire-gauze. The mass had a dark chocolate colour and some solid had separated. The resulting products were the same and the yield also was the same, 1·1 g.

(*ii*) *With a trace of a single base.*—Two experiments with a trace of pyridine in one and a trace of piperidine in the other (1 : 1 : 0·15 mol.) were then set up. The pyridine-containing flask, heated at 100–04° for 45 minutes gave a mixture of the two anilides, total weight 1·2 g. or 44·8 % yield.

The piperidine-containing flask was heated at 110–14° for one hour and a quarter, and gave 1·9 g. of mostly the yellow form. (Yield 70·9 %.)

Condensation with *m*-nitrobenzaldehyde.—

Two condensations were set up, one with a trace of pyridine and the other with that of piperidine (1 : 1 : 0·15). As the condensation appeared to go well on the water-bath, a higher temperature was not used and the heating was continued only for 75 minutes. The product from both was *m*-nitrocinnamanilide, yellow silky needles (from acetone or alcohol), melting at 194–95°. Yield 1·4 g. (52 %) from the first and 1·8 g. (67 %) from the other. (Found : C = 67·7 %, H = 4·7 % ; N = 10·43 %. $C_{15}H_{12}O_3N_2$ requires C = 67·15 % ; H = 4·47 % ; N = 10·45 %.)

Condensation with *p*-nitrobenzaldehyde.—

p-Nitrobenzaldehyde gave in the same way *p*-nitrocinnamanilide, pale yellow needles, m.p. 208°. Yield, with pyridine, 2 g., 74·6 % ; with piperidine, 1·9 g., 70·9 %. (Found : C = 67·4 % ; H = 4·42 % ; N = 10·5, 10·7 %. $C_{15}H_{12}O_3N_2$ requires C = 67·15 % ; H = 4·47 % ; N = 10·45 %.)

In the table given below, the figures given under I are the highest yields obtained by *us* (not by Ahluwalia, Haq and Ray) by using the mixture method. Under II, the figures are the highest yields obtained by the trace-method, *i.e.*, with a trace of either pyridine in some case, or with that of piperidine in the others.

TABLE.

Aldehyde	I per cent.	II per cent.
Piperonal	Acid 32	Acid 3·7
	Anilide 7·4	Anilide 56·2
Salicylaldehyde	Acid 0·0	Acid 0·0
	Anilide 30·2	Anilide 37·8
m-OH Benzaldehyde	,, 67	,, 79·6
p-OH ,, ...	,, 62·7	,, 79·6
Benzaldehyde	,, 80·7	,, 89·2
o-NO_2 Benzaldehyde	,, 41·0	,, 70·9
m-NO_2 ,, ...	Not tried	,, 67·0
p-NO_2 ,, ...	,,	,, 74·6
p-Tolylaldehyde	,,	,, 71·0

SUMMARY.

1. Malonanilic acid has been condensed with several aromatic aldehydes and a comparative study is made of the yields obtained by (*i*) the method of using pyridine in large excess together with a trace of piperidine and (*ii*) the method of using only a trace of *either* of the two.

2. The yields obtained by applying method (*i*) as Ahluwalia, Haq and Ray have done, are increased further by some modifications adopted in his paper. But even the highest yields so obtained, are lower than those obtained by the application of method (*ii*).

3. Incidentally, therefore, the utility of method (*ii*), observed in condensations of aldehydes with malonic acid, is thus extended further.

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THE CONDENSATION OF ALDEHYDES WITH AMIDES.

Part II. The Condensation of Cinnamaldehyde.

By Rup Kishore Mehra and Kantilal C. Pandya.
(*From the Department of Chemistry, St. John's College, Agra.*)

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As far as we are aware, there has been only one such condensation reported, and that is by Gupta,[1] of cinnamaldehyde with phenylacetamide, brought about without any condensing or catalytic agent, by merely heating the two together, and resulting in the production of cinnamylidene-bisphenylacetamide. In the present paper, the condensations of this aldehyde are studied with four amides, namely, phenylacetamide, acetamide, propionamide and benzamide, under several different conditions of temperature, molecular proportions and catalytic influences. The condensations in all cases take place and produce the cinnamylidene-bisamides. The yields are fair and at times good, but are not generally as good as were noted with salicylaldehyde in Part I.[2] The bisamides have always to be freed from unused cinnamaldehyde and resinous products: this, though obviously lowering the yield, is easily accomplished by means of alcohol.

The yields have often increased considerably by judicious variations in the period of heating or the temperature, or even by taking an excess of the amide. Indeed, it is clear that, in the present case at least, the improvement in the yield is dependent more on the suitable observation of these conditions than on the presence or the absence of an organic base as a catalyst. The best yield has at times been obtained in the absence of any base. It is not improbable that the presence of even a trace of a base may promote side-reactions such as polymerisation, or condensation-polymerisation, which must be particularly likely in the case of an unsaturated aldehyde like this. The cinnamaldehyde recovered from these condensations was deeply coloured and could not well be used again.

As Gupta[1] does not mention any yield, his condensation has been repeated and the yield is found to be only about 15 %. This improves only slightly to 18 %, by an alteration in the heating.

The cinnamylidene-bisacetamide, m.p. 234°, is obtainable in the maximum yield of over 50 %. Many alterations in the conditions of the condensation had to be tried before this result was arrived at (*vide* tables).

Cinnamylidene-bisbenzamide was a little more readily obtained, in the maximum yield of 55 %, m.p. 250°.

The aldehyde condensed also with propionamide, when the corresponding bisamide was obtained in yields of about 50 %.

The condensation of cinnamaldehyde with formamide also takes place and has been studied, but has not been mentioned in the experiments, because the solid amorphous substance obtained could not be very well purified in so far as a good melting-point has not been obtained. Curiously, however, several N-determinations give very consistent values. These values, however, are much lower than those calculated for possible condensation-products. The substance has, therefore, to be investigated further.

Under the expectation that hydrocinnamaldehyde being saturated, might give a better yield, one experiment on its condensation was performed and is recorded. It is found to condense with benzamide, when the two are heated together, but some benzamide and some aldehyde are recovered unchanged, and the yield of the dihydrocinnamylidene-bisbenzamide is about 40 %.

Experimental.

Condensation of cinnamaldehyde with phenylacetamide.—

Gupta's experiment being repeated, 3·5 g. of cinnamaldehyde and 6·9 g. phenylacetamide (1 : 2 mol.) on heating under reflux at 160–70° for two hours gave 1·5 g. of the bisamide, melting at 238°.

Other experiments were tried as described in the Table below : the maximum yield of 18·7 % was obtained by a modification in the conditions as under :—

TABLE I.

Molecular Proportions Aldehyde : Amide : Pyridine	Temperature	Time of Heating	Yield	
			Weight	Per cent.
1 : 1 : 0·0	160–70°	2 hours	0·6 g.	6·2
1 : 2 : 0·0	,,	,,	1·5 g.	15·6
1 : 2 : 0·05	,,	,,	,,	,,
,,	130–40°	3 hours	,,	,,
1 : 2 : 0·0	,,	,,	1·8 g.	18·7

As the presence of pyridine did not influence the yield in the ordinary way, other bases and different conditions were not tried in this case.

Condensation of cinnamaldehyde with acetamide.—

3·5 g. cinnamaldehyde and 1·5 g. dry powdered acetamide (1 : 1 mol.) were heated in a small flask on the water-bath for six hours. The product separated in fine crystals even when the flask was still warm. On cooling the mixture was taken out in a mortar and ground well with hot alcohol to dissolve the unchanged aldehyde. It was filtered on cooling, washed with cold alcohol, and recrystallised from hot alcohol. Fine milk-white needle crystals, of cinnamylidene-bisacetamide, m.p. 234°, were obtained. Yield 0·8 g. (13·8 %). (Found : N = 11·7, 11·6 %. $C_{13}H_{16}N_2O_2$ requires N = 12·07 %.)

Various modifications in the conditions were tried to improve the yield, the most important of which are given in the Table below. On the addition of a trace of pyridine, as well as with other changes in the manner of heating, the yield increased only to 0·9 g. or to 15·5 %. It was obvious that for obtaining the bisacetamide, the molar proportions should be 1 : 2. This change was made, and the yield improved, under different conditions and ranged from 25 to 43 % of theory. It was observed that some acetamide

TABLE II.

Proportions Mol. Aldehyde : Amide : Pyridine	Temperature	Time of Heating	Yield	
			Weight	Per cent.
1 : 1 : 0·0	Water-bath	6 hours	0·8 g.	13·8
1 : 1 : 0·15	,,	,,	0·9 g.	15·5
1 : 1 : 0·0	120–25°	2 ,,	,,	,,
1 : 2 : 0·0	Water-bath	8 ,,	1·5 g.	25·3
,,	110–15°	4 ,,	,,	,,
,,	120–25°	2 ,,	1·7 g.	28·8
1 : 2 : 0·15	,,	4 ,,	,,	,,
1 : 2 : 0·0	100–10°	24 ,,	2·5 g.	43·1
1 : 3 : 0·0	110–15°	10 ,,	2·7 g.	46·5
1 : 4 : 0·0	120–25°	2 ,,	,,	,,
1 : 4 : 0·15	,,	4 ,,	3·0 g.	51·7

used to volatilise away and that some was left behind and could be recovered with some of the aldehyde. Temperatures higher than 125° induced charring: so did much prolonged heating. The next experiments were tried with 3 mols. of the amide for one of the aldehydes and the yield slightly increased, ranging from 38 to 46 %. With 4 mols. of acetamide, the yield went up to 51·7 %.

Condensation of cinnamaldehyde with benzamide.—

The condensation was carried out in the usual manner. It was necessary to use higher temperatures. The highest yield with 1 : 1 mol. proportions was 40 % and with 1 : 2 mol. 55 %. Cinnamylidene-bisbenzamide, recrystallised from hot alcohol, came out as a white micro-crystalline substance with a m.p. at 250°. It was insoluble not only in water but also in methyl alcohol, acetone, benzene and carbon bisulphide: very slightly soluble in cold alcohol, and a little more in hot.

Nitrogen, Found: 8·5 %. $C_{23}H_{20}N_2O_2$ requires N = 7·9 %.

TABLE III.

Molar Proportions Aldehyde : Amide : Pyridine 3·3 g.	Temperature	Time of Heating	Yield	
			Weight	Per cent.
1 : 1 : 0·0	110°	8 hours	1·5 g.	16·9
1 : 1 : 0·15	,,	,,	,,	,,
,,	115–120°	10 ,,	1·7 g.	19·1
1 : 1 : 0·0	140–145°	2 ,,	2·1 g.	23·6
1 : 1 : 0·15	110–120°	9 ,,	2·9 g.	32·6
1 : 1 : 0·0	115–120°	9 ,,	3·6 g.	40·4
1 : 2 : 0·0	100–110°	8 ,,	1·7 g.	19·1
,,	140–145°	2 ,,	2·5 g.	28·1
,,	115–120°	9 ,,	4·5 g.	50·5
,,	140° and 110°	2 ,, 6 ,,	4·5 g.	50·5
1 : 2 : 0·15	,,	,,	4·9 g.	55

Condensation of cinnamaldehyde with propionamide.—

3·3 g. aldehyde, 3·6 g. propionamide and 0·2 c.c. pyridine were heated on the water-bath for 8 hours. The product was extracted and purified as usual. Milk-white needles, m.p. 220–21°. Yield 3·0 g. (46 %).

The same heated in the same way but without pyridine, gave a slightly greater yield, 3·3 g. (50·9 %).

Cinnamylidene-bispropionamide gave N = 10·5 %. $C_{15}H_{20}N_2O_2$ requires N = 10·8 %.

Condensation of hydrocinnamaldehyde with benzamide.—

3·2 g. of the hydrocinnamaldehyde and 6 g. of benzamide (1 : 2 mol.) were heated alone without pyridine for 2½ hours at 140–50°. The product extracted and purified as usual came out as a white micro-crystalline powder, m.p. 244–45°. Yield 3·5 g. (39·1 %).

The bisbenzamide gave N = 7·9 %. $C_{23}H_{22}N_2O_2$ requires N = 7·8 %.

Summary.

1. Cinnamaldehyde has been condensed with four amides, in the presence of a trace of pyridine as well as in the absence of any reagent. The yields are on the whole good. The presence of the base does not very much affect the yield.

2. The product in all cases is the cinnamylidenebisamide.

3. Similarly hydrocinnamaldehyde is also condensed with benzamide and gives a fair yield of the bisamide.

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THE CONDENSATION OF ALDEHYDES WITH MALONIC ACID IN THE PRESENCE OF ORGANIC BASES.

Part X. The Condensation of 2 : 4-Resorcylaldehyde.

By Kantilal C. Pandya and Tejpal Singh Sodhi.
(From the Department of Chemistry, St. John's College, Agra.)

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In the condensation of aromatic aldehydes with malonic acid in the presence of organic bases, attention has already been drawn to the remarkable influence which a hydroxy-group on the aromatic nucleus exerts on the condensation. It hinders or inhibits the reaction, reducing the yields to a very small amount or even to nil.[1] Dutt,[2] who also made the observation, tried to get over it by employing carbethoxy-derivatives of the hydroxy-aldehydes. The yields were still bad. Kurien and Pandya[3] then found that yields of over 50% could be obtained in the case of salicylaldehyde, when pyridine was taken in a trace only : this observation was extended by Azhar, Kurien and Pandya[4] who showed that traces of some other bases were equally or even more effective, while if the base was in larger proportions, the condensation altogether failed. The highest yield obtained from salicylaldehyde was 77%,[4] and the *p*-hydroxybenzaldehyde gave 64%.[5] The *m*-isomer showed, at least in this series, the least disturbance and no diminution, as it gave a theoretical yield.[6] The yields in the cases of the *o*- and the *p*-hydroxybenzaldehydes approached even the quantitative, when the hydroxy group was replaced, not by the carbethoxy,[2] but by the methoxy group : the *o*-, *m*- and *p*-methoxybenzaldehydes gave almost quantitative yields.[7]

From this experience it would be expected that if the aromatic aldehyde contains more than one hydroxy-group on the nucleus, a further diminution of the yield might take place. In 2 : 4-resorcylaldehyde, the two hydroxy-groups are *o*- and *p*- to the aldehyde group, and the yields, under the best of conditions, are actually lower than were obtained with salicylaldehyde and *p*-hydroxybenzaldehyde, namely only 43% of umbelliferone. This was obtained with a trace of pyridine, the yield with a trace of piperidine being lower, namely 24 %.

Perkin's reaction has also been applied to this aldehyde, by Tiemann and Lewy,[8] who obtained first 7-acetoxycoumarin, which could be changed

into umbelliferone or umbellic acid by hydrolysis with alkali. This experiment was repeated and the yield of umbellic acid obtained was about 26 %.

The condensation takes place even in the absence of any reagent, and is found to give umbellic acid, 33 %. When a base is present the substance forms umbelliferone and not umbellic acid.

Robinson and Shinoda's method[9] was applied, but it failed entirely, the mixture becoming black and tarry, and no umbelliferone could be taken out.

This led us to try Stuart's method,[10] of heating the aldehyde with malonic acid and glacial acetic acid, and this gave about 54 % yield of umbellic acid.

It may be noted that Dey, Rao and Sheshadri[11] have prepared umbelliferone from resorcinol and malic acid by means of Pechmann's reaction. The yield of umbelliferone is, however, only 25 % of theory.

The results of the condensation of protocatechuicaldehyde are in a line with the above and will be included in the next part of the series.

Experimental.

Condensation in the presence of a trace of piperidine.—1·4 g. resorcylaldehyde, 1 g. malonic acid and 0·13 c.c. of piperidine were heated on the water-bath for about five hours. The colour of the mixture became soon dark brown and bubbling was seen. The whole mass, after cooling overnight, was extracted with sodium carbonate solution. The alkali extract showed a beautiful violet fluorescence. It was filtered, and the filtrate on acidification gave a brown solid, weighing 0·4 g.

The same experiment was repeated at 105–10°, but the yield remained the same.

Condensation with a trace of pyridine.—The same amounts with 0·12 c.c. of pyridine (1 : 1 : 0·15 mol.) treated in the same way, gave, on water-bath, 0·6–0·7 g.

Two other experiments, made so that the heating was carried out at 100 05°, and 105-10° respectively, made no improvement in the yield.

The umbelliferone so obtained, purified by methyl alcohol (animal charcoal) came out as colourless prisms, m.p. 225°. (Colour could not always be removed, as in the case of the products of the other condensations.) It gave a marked fluorescence with ammonia, as described by Sommer[12] and Tiemann and Reimer.[13] It reduced ammoniacal silver and gave a reddish brown colour with aqueous ferric chloride.

Condensation without any reagent.—2-8 g. resorcylaldehyde, and 2 g. malonic acid were heated alone as above. The product, after extraction,

was a light brown powder, umbellic acid. On purification, it became yellow, did not melt, but decomposed at 240° (*cf.* Posen[14]). It weighed 1·2 g. or 33 %.

Tiemann and Lewy's condensation.—2·8 g. resorcylaldehyde, 1·6 g. anhydrous sodium acetate and 6 c.c. acetic anhydride were heated in a flask, with a reflux condenser, at 160–80° for 8 hours. The colour of the mass changed to brown. The product extracted, as usual, weighed 1·4 g. It was 7-acetoxycoumarin, of a brown colour and melted at 140°. Hydrolysed by refluxing with 10 % KOH solution, 3 g. gave 2 g. of umbellic acid.

Robinson and Shinoda's method.—1·3 g. aldehyde, 3 g. malonic acid, 2·8 c.c. pyridine with 3–4 drops of piperidine were heated on a water-bath for 90 minutes and on a wire-gauze for 20 minutes. The whole mass had become black, and gave nothing by the usual treatment.

Condensation by Stuart's method.—3 g. resorcylaldehyde, 3 g. malonic acid and 2 g. glacial acetic acid were heated on a water-bath for ten hours. The mass had become deep pink on the addition of the acetic acid and soon became liquid, which assumed a deep red, and finally a violet colour. Bubbling was continuous, and at the end, the umbellic acid was taken out as usual, and weighed 2·1 g. (53·6 %).

Summary.

2 : 4 Resorcylaldehyde undergoes condensation with malonic acid giving umbelliferon or umbellic acid according to the conditions. The yield is as expected lower than the lowest obtained with mono-hydroxybenzaldehydes.

A trace of pyridine gives better yield than any method, except that the yield is slightly higher when glacial acetic acid is used in place of a base.

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ON THE AMYLASE FROM THE INDIAN WATER CHESTNUT (*TRAPA BISPINOSA* ROXB.).

Part II. Studies with the Purified Powdered Form of the Enzyme.

By Deoki Nandan Jain and Radha Raman Agarwal.
(*From the Chemistry Department, Agra College and St. John's College, Agra.*)

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In a previous communication, Agarwal[1] showed that the fruits of *Trapa bispinosa*, Roxb. (Vern. Singhara, Paniphal or Sringataka) contain an active diastatic enzyme and isolated an aqueous extract which gave very interesting results on starch. The optimum pH of the amylase was found to be 5·2–5·6, and the optimum temperature 50–55° C. The amylase was further shown to be mainly a saccharogenic-β-amylase decomposing starch upto the maltose stage. In the present paper the kinetics of the hydrolysis of starch, by means of a highly purified powdered form of the enzyme, obtained by repeated dialysis of the extract, precipitation by 90% ethyl alcohol and sedimentation by a powerful centrifuge have been investigated. It has been found that the optimum temperature of this enzyme is at 45–50° C. and optimum pH at 5·2–5·6. The hydrolysis of the starch does not follow the monomolecular course until the decomposition has proceeded for about 90 minutes and even then had a tendency to fall off.

Experimental.

Preparation of the Enzyme Powder.—A fresh supply of the white kernels of *Trapa bispinosa* fruits were obtained and boiled with enough water till the sweetness was increased to its maximum. This operation took about five hours. They were then chopped into small pieces and dried in the shade. The dried pieces were very finely powdered in a machine and sieved. This powder was then soaked in four times its weight of distilled water at pH 5·6 (phosphate buffers) containing a little toluene for about a week. At the end of this period the aqueous extract was filtered first through muslin and then through a filter paper. The extract thus obtained was found to be very rich in amylolytic activity. It was then dialysed in parchment paper against distilled water for about forty hours, the water being renewed twice every day. The amylolytic power was thus increased considerably. After

the dialysis the extract was treated with four times its volume of 90% ethyl alcohol and kept for about four hours in a frigidaire, whereby the enzyme separated in a fine gelatinous form. This was then centrifuged and the sedimented portion separated from the supernatant liquid. The precipitate was redissolved in about 100 c.c. of water, centrifuged, the supernatant liquid removed and again precipitated by alcohol. These operations were repeated at least ten times when the enzyme was obtained in a form which could be filtered with little difficulty over a filter-pump. The filtered enzyme powder was next washed with absolute alcohol and then with ether and finally dried in vacuum over anhydrous calcium chloride. (Yield : 4 g. from 40 Kg. of the fruits, *i.e.*, 0·01%.)

The enzyme powder was of a cream white colour giving a very small residue on burning in a platinum dish. It smelt of carbohydrates and dissolved in water to give a clear solution. It could be kept in stoppered bottles for months without losing any of its amylolytic power.

Methods of Procedure.—Soluble starch (Kahlbaum, extra pure, prepared according to Zulkowsky) was used as a substrate, generally a 2% or 1·5% solution being employed. Hydrogen-ion concentration of the reaction mixture was adjusted by adding Walpole acetate buffers. The effect of pH on the reaction velocity was also studied by using a single buffer solution, *viz.*, Mc Ilvaines citrate buffer. The enzyme solution was obtained by taking a weighed quantity of the enzyme powder, dissolving it in water and making the volume 100 c.c. in a measuring flask. This was used up the same day and prepared afresh for subsequent experiments. The reactions were all carried out in conical flasks at constant temperature in an electrically regulated thermostat. The course of the reaction was studied by removing aliquots of 10 c.c. at definite intervals of time and estimating the amount of reducing sugars formed by the method of Willstätter and Schudel.[2] The velocity constant for a uni-molecular reaction was calculated according to Euler and Svanberg[3] by applying the formula $K = 1/t \log_{10} a/a - x$. In this formula '$a$' has been taken in terms of the total quantity of reducing sugars that can be obtained from the starch using the same quantity of the enzyme powder (0·660 g., 0·654 g., 0·654 g., 0·649 g., of maltose per g. of starch : mean value 0·654 g.).

To Study the Course of the Reaction.—50 c.c. of a 2% starch solution, 10 c.c. of the Walpole acetate buffer (pH 5·67), 25 c.c. of a 0·02% amylase solution and 15 c.c. of water were maintained in the thermostat at 30 ± 0·05° C. Aliquots of 10 c.c. were removed and added to 5 c.c. of the iodine solution (N/10) to stop the action, and the reducing power was estimated. Table I gives the results thus obtained :—

TABLE I. $a = 36{\cdot}3$ c.c. of N/100 thio.

Time (Min.)	Thio-sulph. used in the titration c.c.	x	$K = 1/t \log_{10} \times a/a - x$
15	36·05	9·35	·00862
30	35·05	10·35	·00486
45	33·85	11·35	·00362
60	31·80	13·60	·00340
75	31·30	14·10	·00285
90	30·30	15·10	·00260
105	29·10	16·30	·00247
120	28·35	17·05	·00230

From the above results it is clear that the value of K drops steadily with time but during the period 75 minutes to 120 minutes the fluctuation is not very much. This time was, therefore, further studied.

TABLE II. $a = 18{\cdot}15$ c.c. of N/100 thio.

Time (Min.)	x in c.c. of N/100 thio	$K = 1/t \log_{10} \times a/a - x$
80	7·00	·00233
90	7·15	·00242
95	7·25	·00230
100	7·60	·00235
105	7·65	·00226
110	8·20	·00237
115	8·25	·00229
120	8·70	·00236

The above table clearly shows that the value of the velocity constant K is nearly constant between the time 90 to 120 minutes. In all these subsequent studies the mean values of such determinations have been taken.

The Effect of pH on the Reaction Velocity.—50 c.c. of 2% starch solution, 20 c.c. of the Mc Ilvaines citrate buffers of different pH, 25 c.c. of a 0·02% enzyme solution and 5 c.c. of distilled water were taken at a constant temperature 30 ± ·05° C. 10 c.c. of this reaction mixture were added to 5 c.c. of an N/10 iodine solution and the reducing power estimated.

pH ..	4·2	4·6	5·0	5·4	5·8	6·2	6·6	7·0
K × 10^4	20·49	21·21	23·86	22·00	19·7	19·6	17·30	13·28

The above experiments were repeated by using Walpole's acetate buffers.

pH	3·6	4·0	4·4	4·8	5·2	5·6
K × 10^4	19·81	20·30	20·54	20·88	25·30	22·90

From the above results it is clearly seen that the optimum pH of the enzyme lies between 5·2–5·6.

The Effect of Temperature on the Reaction Velocity.—50 c.c. of a 2% starch solution, 20 c.c. of the Walpole acetate buffer (pH 5·2), 5 c.c. of distilled water and 25 c.c. of the 0·02% enzyme powder were taken in a conical flask and the reaction mixture maintained at different temperatures. 10 c.c. aliquots were removed after the reaction had proceeded for 90 minutes and the velocity constants determined.

Temp. (°C.)	20	25	30	35	40	45	50	55	60
K × 10^4 ..	16·63	19·80	25·30	27·34	31·34	34·20	38·50	25·05	20·10

The above results clearly show that the best temperature for the action of the enzyme is between 45–50° C.

The Effect of Varying the Concentration of the Substrate.—50 c.c. of the starch solution of different concentration (3%–0·5%), 20 c.c. of the acetate buffer (pH 5·2) and 25 c.c. of distilled water were maintained at 30 ± 0·05° C. After 90 minutes 10 c.c. of the reaction mixture were removed and the velocity constant determined.

g. of Starch per 100 c.c. of the reaction mixture ..	1·5	1·25	1·00	0·75	0·50	0·25
K × 10^4 ..	16·48	19·20	25·30	27·72	38·47	103·20

Discussion.

Regarding the course of the hydrolysis of starch by amylase, Euler and Svanberg[3] found that the course is monomolecular only uptil 40–50% of the reaction has proceeded and on further hydrolysis the rate of the reaction diminishes. Willstätter, Graser and Kuhn[4] later on found that in the case of invertase the hydrolysis of sucrose follows this monomolecular course only if the reaction is done at pH 6·7. They also came to the conclusion that very often an enzyme follows this law only for a part of its course. Long before this, however, in the case of the hydrolysis of starch by malt amylase Brown and Glendinning[5] had found that the velocity constant calculated on the basis of the monomolecular law gives a constant only after the hydrolysis has proceeded for about sixty minutes and even then falls off after some time. In this connection it is very gratifying to note that similar results have been obtained with *Trapa* amylase and the reaction velocity calculated from the unimolecular law, though fairly constant after the reaction has proceeded for about 90 minutes, has still the tendency to fall off steadily. This is probably due to the destruction of the enzyme in the course of the reaction which therefore, adds to the slowing down of the reaction, since the concentration of the amylase is very small in comparison with the concentration of the starch, being in the ratio of 1 : 200.

If the concentration of the substrate be varied the reaction velocity at first increases, then reaches a maximum and finally decreases. Generally, the curve relating reaction velocity and substrate concentration is concave downwards. This has been verified for malt amylase by Sjoberg and Ericcson[6] and Eadie.[7] The results obtained with the *Trapa* amylase clearly show that the greatest velocity has been obtained at 0·25% concentration, within the range 1·5–0·25% starch concentration.

The pH optima of this amylase has been found at 5·2–5·6. Generally the pH optima for amylases from vegetable origin lie between 5 and 6. Thus Giri[8] found that the pH optimum for the sweet potato amylase is at 5·5, and that for the malt amylase at 5·2 (Myrback[9]). The optimum temperature was found to be at 45–50° C. The optimum temperature for sweet potato amylase is at 50–55° C. and that of germinating grains 50–56° C. (Patwardhan[10]).

Summary.

A pure powdered form of the amylase has been isolated from the fruits of *Trapa bispinosa* Roxb. and the course of its action on starch has been studied. The velocity constants calculated on the basis of monomolecular reaction give a constant value only after the reaction has proceeded for about 90 minutes. The greatest velocity was found at 0·25% starch concentration. The optimum pH was at 5·2–5·6 and the optimum temperature at 45–50° C.

The authors are indebted to Professor K. C. Pandya and Professor B. L. Vaish, for their valuable advice and interest.

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A GENERALISATION OF LEUDESDORF'S THEOREM.

By Hansraj Gupta.
(From the Government College, Hoshiarpur.)

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1. By an elegant method, Raju[1] has proved certain congruence properties of elementary symmetric functions of numbers less than and prime to m. He has, however, placed certain restrictions on m, which take away much from the beauty of his results. My main object in this paper is to remove these restrictions and prove some universal theorems. I use methods which are more direct and yet as simple as those of Raju.

2. *Notation.*—All small letters denote integers $\geqslant 0$, unless stated otherwise; p's denote primes $\geqslant 2$; $m > 2$, and $h = \phi(m)$.

$A = a_1, a_2, a_3, \cdots a_h$; is the least positive reduced system of residues of m. G_r or $G_r(A)$ denotes the sum of the products of the a's taken r at a time; $0 \leqslant r \leqslant h$. We take $G_0 = 1$.

$G_r(\xi A)$ stands for $G_r(\xi a_1, \xi a_2, \xi a_3, \cdots, \xi a_h)$.

If $m \equiv 0 \pmod{p^u}$, but $\not\equiv 0 \pmod{p^{u+1}}$; $u \geqslant 1$;

then we say that m is u-potent in p, and write $\mathrm{Pot}_p(m) = u$.

If $g \equiv 0 \pmod{\phi(p^\alpha)}$, but $\not\equiv 0 \pmod{\phi(p^{\alpha+1})}$; $\alpha \geqslant 1$; then we say that g is α-piquant in p, and write $\mathrm{Piq}_p(g) = \alpha$.

If $\mathrm{Piq}_p(g) = \alpha$, $\alpha \geqslant 1$, we write M_g for the product $\Pi\left(p^{\alpha + \left[\frac{2}{p}\right]}\right)$, and N_g for the product $\Pi\left(p^{1 + \left[\frac{2}{p}\right]}\right)$. Thus $M_6 = 7 \cdot 3^2 \cdot 2^3$, and $N_6 = 7 \cdot 3 \cdot 2^2$.

S_r or $S_r(A)$ is the sum of the r-th powers of the a's.

3. We make use of the following:

Lemma.—If $\mathrm{Piq}_p(g) = \alpha$, then numbers ξ prime to p, exist such that $\mathrm{Pot}_p(\xi^g - 1) = \alpha + \left[\frac{2}{p}\right]$.

Numbers ξ exist such that $\mathrm{Pot}_p(\xi^q - 1) = \alpha + \left[\frac{2}{p}\right]$, where $q = \phi(p^\alpha)$.

Let $g = qs$, where $p \nmid s$.

Then since $(\xi^g - 1)/(\xi^q - 1) = 1 + \xi^q + \xi^{2q} + \cdots + \xi^{(s-1)q} \equiv s \left(\mathrm{mod}\ p^{\alpha + \left[\frac{2}{p}\right]}\right)$,

we have $\mathrm{Pot}_p(\xi^g - 1) = \mathrm{Pot}_p(\xi^q - 1) = \alpha + \left[\frac{2}{p}\right]$.

4. THEOREM 1.—$2\,G_{2k+1} \equiv (h - 2k)\, m\, G_{2k}, \pmod{m^3}$.

We have

$$\prod_{i=1}^{h} (x + a_i) = \prod_{i=1}^{h} (x + m - a_i).$$

Therefore $$\sum_{r=0}^{h} G_r\, x^{h-r} = \sum_{r=0}^{h} (-1)^r G_r \cdot (x + m)^{h-r}.$$

Equating the coefficients of odd powers of x, we get

$$2\,G_{2k+1} = \binom{h-2k}{1} m G_{2k} - \binom{h-2k+1}{2} m^2\, G_{2k-1} + \cdots + \binom{h}{2k+1} m^{2k+1} G_0.$$

Since $m > 2$, h is even, and we have

$$G_{2k+1} \equiv 0 \pmod{m},\ k \geqslant 0.$$

In particular $$G_{2k-1} \equiv 0 \pmod{m},\ k \geqslant 1.$$

Hence the theorem.

5. THEOREM 2.—$(m, M_g)\ G_{2k}\ (A) \equiv 0 \pmod{m}$; where $g = (2k, h)$; $k > 0$.

If $\mathrm{Pot}_p\ (m) = u$, and $\mathrm{Piq}_p\ (g) = \alpha$,

then for each p/m, we have to prove that

$$G_{2k}\,(A) \equiv 0 \left(\mathrm{mod}\ p^{u-\alpha-\left[\frac{2}{p}\right]}\right). \tag{1}$$

Let ξ be an integer such that

$$\mathrm{Pot}_p\,(\xi^{2k} - 1) = \alpha + \left[\frac{2}{p}\right].$$

Such an integer exists unless $\mathrm{Piq}_p\,(2k) > u - \left[\frac{2}{p}\right]$.

In the latter case $\alpha = u - \left[\frac{2}{p}\right]$, and (1) evidently holds.

If $\alpha < u - \left[\frac{2}{p}\right]$; we have

$$\xi^{2k}\, G_{2k}\,(A) = G_{2k}\,(\xi A) \equiv G_{2k}\,(A) \pmod{p^u};$$

or $(\xi^{2k} - 1)\, G_{2k}\,(A) \equiv 0 \pmod{p^u}$;

and therefore $G_{2k}\,(A) \equiv 0 \left(\mathrm{mod}\ p^{u-\alpha-\left[\frac{2}{p}\right]}\right)$.

The theorem follows immediately from this.

Since $\mathrm{Pot}_p\ (g) = \alpha - 1$, $\mathrm{Pot}_p\ (h - 2k) \geqslant \alpha - 1$;

therefore as a direct consequence of Theorems 1 and 2, we get

$$2\,(m, N_g)\, G_{2k+1}\,(A) \equiv 0 \pmod{m^2},\ k \geqslant 1. \tag{2}$$

This is my generalisation of Leudesdorf's Theorem.

6. The following particular cases of (2) are noteworthy:

Let $2k = h - 2$, then $g = 2$, and $N_g = 12$.

Hence $2\ (m, 12)\ G_{h-1} \equiv 0 \pmod{m^2}$.

This is Leudesdorf's Theorem.[2]

Let $2k = h - 4$, then $g = 2$ or 4, and $N_4 = 60$.

Hence $2\ (m, 60)\ G_{h-3} \equiv 0 \pmod{m^2}$.

7. THEOREM 3.—$2\ (m, M_g)\ S_{2k+1} \equiv 0 \pmod{m^2}$; where $g = (h, 2k), |\ k\ | > 0$.

Theorem 2 is true if G is replaced by S.

Moreover, we have

$$2S_{2k+1} \equiv \sum_{i=1}^{h} \left\{ a_i^{2k+1} + (m - a_i)^{2k+1} \right\}$$

$$\equiv (2k + 1)\, m\, S_{2k} \pmod{m^2}.$$

Hence the theorem.

Since $a_i^{-t} \equiv a_i^{\lambda h - t} \pmod{m}$,

the theorem of this section is true for all integral values of k ; $k \neq 0$.

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2. For another proof see Gupta, H., " A Generalisation of a Theorem of Wolstenholme," *Math. Notes, Edinburgh Math. Soc.*, 1935, **29**, 11–13.

A STUDY OF THE SYSTEMS $CuSO_4$–$NiSO_4$–H_2O AND $CuSO_4$–$CoSO_4$–H_2O.

By T. S. Suratkar, S. M. Mehta
and
Mata Prasad.
(*From the Chemical Laboratories, Royal Institute of Science, Bombay.*)

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Prasad and Tendulkar[1] have shown that the nickel-copper matte obtained by roasting the nickel ore contains most of the nickelous oxide in the passive state. Consequently when the matte is treated with dilute sulphuric acid nearly the whole of copper oxide and very little of nickel oxide go into solution. These authors have also suggested that the small amount of nickel in solution may be due to (*i*) the presence of small quantities of nickelic oxide in the matte and (*ii*) the action between nickel oxide and aqueous solution of copper sulphate. However, another factor which may influence the relative amounts of copper and nickel salts in the leached solution is the mutual effect of the solubilities of nickel and copper sulphates.

A search of literature revealed that although the system alkali sulphate—nickel sulphate—water has been studied in great detail practically no data is available on the study of the system $CuSO_4$—$NiSO_4$—H_2O. Mitscherlich[2] found that monoclinic or triclinic crystals separate out of a solution containing both the salts depending upon their relative proportions. Fock[3] gave more details about the conditions under which the two types of crystals are obtained and confirmed the observations of Mitscherlich. Double sulphates having the formula $CuSO_4 \cdot 2NiSO_4 \cdot xH_2O$ have been obtained from mixed solutions of the component salts by Etard,[4] Dufet,[5] Boisbaudran[6] and Hauer.[7]

In order to investigate the effect of adding increasing quantities of copper sulphate on the solubility of nickel sulphate, the system nickel sulphate,

[1] *J.C.S.*, 1931, 1407.
[2] *Pogg. Ann.*, 1827, **11**, 326 ; 1828, **12**, 146.
[3] *Zeit. Kryst.*, 1897, **28**, 385.
[4] *Compt. Rend.*, 1878, **87**, 602.
[5] *Ibid.*, 1878, **86**, 880.
[6] *Ann. Chim. Phys.*, 1869, **18(4)**, 288.
[7] *Pogg. Ann.*, 1865, **125**, 638.

copper sulphate and water, was studied at 40°. A study of the system, cobalt sulphate, copper sulphate and water, was a natural sequel and it was also investigated in the same manner and at the same temperature as the above-mentioned system. This system has been investigated by Crockford and Brawley[8] at 0° and 25°. They found that at both these temperatures the solids consist of $CuSO_4$, $5H_2O$ and a series of solid solutions in which the copper salt is partially replaced by $CoSO_4$, $7H_2O$.

Experimental.

It was ascertained that 40 g. of nickel sulphate, 35 g. of cobalt sulphate and 20 g. of copper sulphate are more than sufficient to form saturated solutions in 25 c.c. of water. These chemicals were Kahlbaum's extra pure substances and were used after testing their purity. The different mixtures were kept in well-stoppered glass bottles and shaken in a water thermostat at 40° for more than 90 hours. The metal rack holding the bottles was rotated by means of an electric motor. After shaking the mixture for the above length of time it was assumed that equilibrium was reached. The liquid was separated from the solid phase and it was analysed.

The amounts of copper, nickel and cobalt were estimated by the electrodeposition method using a rotating platinum gauze cathode and a platinum gauze anode. From the weights of the metals deposited the corresponding amounts of the sulphates were calculated. The results obtained for the systems $CuSO_4$—$NiSO_4$—H_2O and $CuSO_4$—$CoSO_4$—H_2O are given in Tables I and II and are represented by means of triangular diagrams given in Figs. 1 and 2.

It will be seen from Table I that when the concentration of copper sulphate increases from 0·00 g. to 8·47 g. (Nos. 1 to 4) the solubility of nickel sulphate decreases from 32·33 g. to 26·10 g. per 100 g. of the solution. Similarly when the concentration of nickel sulphate increases from 0·00 g. to 21·52 (Nos. 9 to 19) the solubility of copper sulphate decreases from 23·00 g. to 11·73 g. per 100 g. of the solution. Nos. 5 to 8 show that the composition of the solution is nearly constant.

Applying the phase rule, $F = C - P + 2$, to the present system it will be seen that there are three components, copper sulphate, nickel sulphate and water and the phases are vapour, solution and either one or two solid hydrates. The system will be bivariant in the first case and univariant in the second; in the latter case the composition of the solution will remain practically constant at constant temperature. The data on the

[8] *J. Phys. Chem.*, 1932, **36**, 1534.

TABLE I.

$CuSO_4$ – $NiSO_4$ – H_2O at 40°.

No.	Liquid			Solid		Solid Phase
	% $NiSO_4$	% $CuSO_4$	% H_2O	% $NiSO_4$	% $CuSO_4$	% H_2O	
1	32·33	..	67·67	55·24	..	44·76	$NiSO_4$, 7 H_2O
2	30·92	2·21	66·87	55·24	..	44·76	,,
3	27·41	6·56	66·03	55·24	..	44·76	,,
4	26·10	8·47	65·43	55·24	..	44·76	,,
5	25·28	9·68	65·04	45·32	11·36	43·32	$NiSO_4$, 7 H_2O and solid solution
6	25·30	9·70	65·00	39·25	18·40	42·35	,,
7	25·10	9·87	65·03	35·22	23·09	41·69	,,
8	25·20	9·90	64·90	31·25	27·69	41·06	,,
9	21·52	11·73	66·75	..	63·94	36·06	$CuSO_4$, 5 H_2O
10	19·86	12·59	67·55	..	63·94	36·06	,,
11	18·18	13·80	68·02	..	63·94	36·06	,,
12	16·85	14·56	68·59	..	63·94	36·06	,,
13	14·74	15·65	69·61	..	63·94	36·06	,,
14	12·71	16·63	70·66	..	63·94	36·06	,,
15	10·37	17·80	71·83	..	63·94	36·06	,,
16	8·57	19·01	72·42	..	63·94	36·06	,,
17	5·42	20·00	74·58	..	63·94	36·06	,,
18	2·70	21·19	76·11	0·22	63·69	36·09	,,
19	..	23·00	77·00	..	63·94	36·06	,,

TABLE II.

System $CuSO_4 - CoSO_4 - H_2O$ at 40°.

No.	Liquid			Solid			Solid Phase
	% $CoSO_4$	% $CuSO_4$	% H_2O	% $CoSO_4$	% $CuSO_4$	% H_2O	
1	31·90	..	68·10	55·16	..	44·84	$CoSO_4$, 7 H_2O
2	30·14	2·00	67·86	52·23	3·39	44·38	,,
3	27·99	3·65	68·36	49·04	7·10	43·86	Solid solution
4	25·00	7·30	67·70	47·57	8·79	43·64	,,
5	23·39	9·06	67·55	46·96	9·51	43·53	,,
6	22·04	10·50	67·46	45·40	11·31	43·29	,,
7	21·44	11·38	67·18	42·53	14·64	42·83	,,
8	19·63	12·50	67·87	37·56	20·40	42·04	Solid solution & $CuSO_4$, 5 H_2O
9	19·34	12·64	68·02	27·72	31·81	40·47	,,
10	19·76	12·46	67·76	0·00	63·94	36·06	$CuSO_4$, 5 H_2O
11	18·18	13·24	68·58	1·22	62·53	36·24	,,
12	16·75	14·45	68·80	0·00	63·94	36·06	,,
13	15·20	15·29	69·51	0·00	63·94	36·06	,,
14	11·51	17·01	71·48	0·44	63·43	36·13	,,
15	9·79	17·96	72·25	0·00	63·94	36·06	,,
16	4·88	20·12	75·00	2·26	61·32	36·42	,,
17	2·55	21·33	76·11	1·19	62·56	36·25	,,
18	..	22·92	77·08	..	63·94	36·06	,,

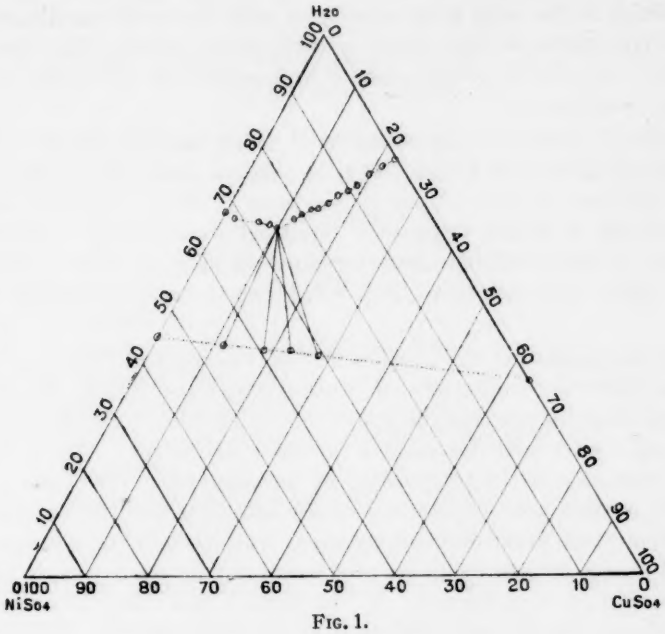

FIG. 1.

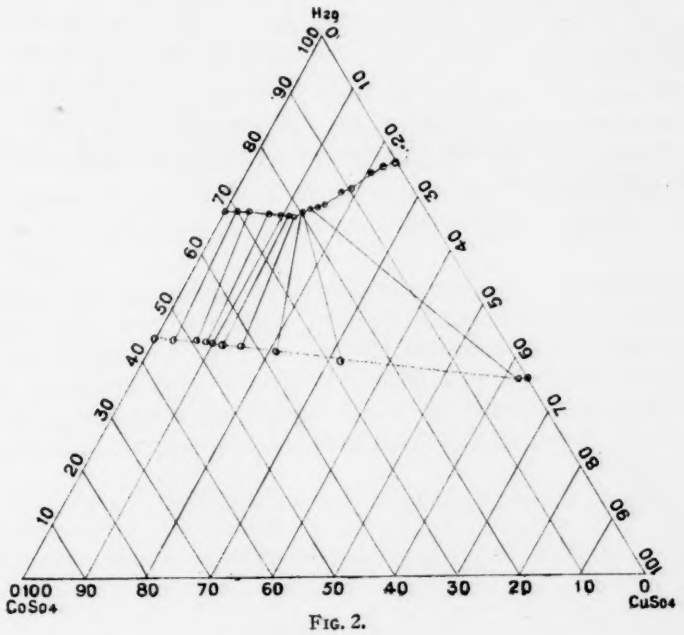

FIG. 2.

composition of the solid is in accordance with the above-mentioned conclusions. The residue in Nos. 1 to 4 consists of only $NiSO_4$, $7H_2O$ and in Nos. 9 to 19 of only $CuSO_4$, $5H_2O$; Nos. 5 to 8 contain the two solid hydrates in varying proportions.

Table II shows that the solubility of cobalt sulphate falls from 31·90 g. to 21·44 g. (Nos. 1 to 7) per 100 g. of solution when the concentration of copper sulphate increases from 0·00 g. from 11·38 g. Similarly when the concentration of cobalt sulphate is increased from 0·00 g. to 18·18 g. the solubility of copper sulphate decreases from 22·92 g. to 13·24 g. (Nos. 11 to 18) per 100 g. of the solution. Nos. 8 and 9 show nearly a constant composition.

The composition of the residues in Nos. 1 and 2 and those in Nos. 10 to 18 shows that they consist of only $CoSO_4$, $7H_2O$ and $CuSO_4$, $5H_2O$, respectively, and that the system is bivariant. Solids in Nos. 8 and 9 contain both copper and cobalt sulphates and the system is univariant. This is supported by the constancy of the composition of the solutions. The solids in Nos. 3 to 7 also contain both copper and cobalt sulphates but the composition of the solution varies in the different mixtures. This leads to the conclusion that the solid phases in these cases are solid solutions and the system is bivariant. The existence of solid solutions in this system has also been found by Crockford and Brawley who studied it at low temperatures. This data also shows that if the solid consists of two phases—one being the hydrated salt and the other solid solution—the composition of the liquid is constant.

Figs. 1 and 2 show that the curves consist of two branches. This shows that there are no possibilities of the formation of double salts of copper sulphate and nickel sulphate and those of copper sulphate and cobalt sulphate under these conditions.

ON LINEAR TRANSFORMATIONS OF BOUNDED SEQUENCES—I.

By K. S. K. Iyengar.

(*From the Department of Mathematics, University of Mysore, Bangalore.*)

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PART I.

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§ 1. *Introduction.*

In a remarkable book devoted to Cesáro's summability method, Anderson[1] has derived a number of very interesting theorems relating to transformations corresponding to differences of any real order of a given sequence. Some theorems of a similar nature (generalizing the notion of monotonicity) are also given by Knopp.[2] It has occurred to me that, such theorems being special types of transformations of sequences, it would be desirable to study properties of transformations of a general nature of subject, of course, to suitable conditions. I have therefore considered here a class of linear transformations (T) given by the infinite matrix $\| a_{mn} \|$ characterised by four conditions, the reciprocals (T^{-1}) of these transformations, and the products of the T and T^{-1}.

Several very interesting results have emerged as a result of these considerations. The most interesting property of the class (T) is *that they all have unique reciprocals with regard to null sequences.* The conditions under which a set of operators, T_1, T_2, $T_3 \cdots$, and T_1^{-1}, T_2^{-1}, T_3^{-1}, $\cdots$ may be validly combined, and the equivalence of one combination with another when applied to bounded or null sequences are also discussed. For example,

[1] A. F. Anderson, *Studier over Cesáro's summabilitet's methode* (Danish). See the second chapter entitled "*Om differences*".

[2] K. Knopp, "*Mehrfach monotone Zahlen*," *Math. Zs.*, 1925, 22, 75–85.

if $\{x_n\}$ be a null sequence, $T_1\,T_2\{T_1^{-1}(x_n)\}$ has, in general, no meaning, whereas $T_2\,T_1\,\{T_1^{-1}(x_n)\} = T_2\,(x_n)$. If we denote by (G) the class of the (T), (T^{-1}) and products of (T) and (T^{-1}), we can say that the *G's are, in general, non-commutative.* These results are comprised in parts one and two.

Part three of this series deals with a sub-class of (T) which we denote by $\overline{U}$, their reciprocals and products such as $\overline{U}_1\overline{U}_2\overline{U}_3\cdots$, $\overline{U}_1\overline{U}_2\overline{U}_3^{-1}\cdots$, etc. Denoting this class by (G_1) it is shown that, in contrast to the G's, *the G_1's are commutative.* Also, the transformations corresponding to differences of any real order form a sub-class of G_1 itself, so that *the theorems of Anderson and Knopp referred to above follow as particular cases of our general theorems* in parts one and two.

A type of transformation corresponding to (T) for application to functions of the continuous real variable is given and corresponding to the existence of a unique reciprocal for a T we have the unique solution of the integral equation

$$u\,(t) + \int_t^\infty u\,(t_1)\,k\,(t_1, t_1)\,dt_1 = \phi\,(t)$$

under the condition $u\,(t) \to 0$, $t \to \infty$ and the Kernel K (t, t_1) being characterised by conditions similar to those imposed on a_{mn}.

§ 2. *Theorem on a Class of Infinite Matrices.*

We shall consider in this paper, the class of linear transformations (T) given by the infinite matrix $\| a_{mn} \|$ characterised by the following four conditions :—

$$\left.\begin{array}{lll} (a) & a_{nn} = 1 & \\ (b) & a_{mn} = 0 & (n < m) \\ (c) & a_{mn} \leqslant 0 & (n > m) \\ (d) & -\sum_{\rho=1}^{\infty} a_{n,\,n+\rho} \leqslant 1 & \end{array}\right\} \qquad (2,\,1)$$

Let $A = \| a_{mn} \|$ be the defining matrix, and $\| \delta_{mn} \|$ the unit matrix. We shall prove the *theorem that there exists a unique matrix B such that B.A. = $\| \delta_{mn} \|$.* Let

$$A = \begin{vmatrix} 1 & a_{01} & a_{02} & \cdot & \cdot & \cdot \\ 0 & 1 & a_{12} & \cdot & \cdot & \cdot \\ 0 & 0 & 1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix} = \begin{vmatrix} 1 & -a_{01} & -a_{02} & \cdot & \cdot & \cdot \\ 0 & 1 & -a_{12} & \cdot & \cdot & \cdot \\ 0 & 0 & 1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix}$$

Conditions (2, 1) imply $a_{mn} \geqslant 0$, and $\sum_{\rho=1}^{\infty} a_{n,n+\rho} \leqslant 1$.

Let $B = \| \beta_{mn} \|$. Then the condition $B \cdot A = 1$ gives

$$\sum_{r=0}^{\infty} \beta_{mr}\, a_{rn} = \delta_{mn}$$

i.e., $\sum_{r=0}^{n} \beta_{mr}\, a_{rn} = \delta_{mn}$, since, from (*b*) of (2, 1) $a_{rn} = 0$ for $r > n$.

Case 1. $n < m$: $(\delta_{mn} = 0)$.

$$\sum_{k=0}^{n} \beta_{mk}\, a_{kn} = \sum_{k=0}^{n-1} \beta_{mk}\, a_{kn} + \beta_{mn}\, a_{nn} = \delta_{mn} = 0.$$

Assuming $\beta_{m0}, \beta_{m1} \cdots \beta_{m,n-1}$ all to be zero, we have

$\beta_{mn}\, a_{nn} = 0$, *i.e.*, $\beta_{mn} = 0$; since $a_{nn} = 1$ from (2, 1) ;

but $\beta_{m0} = 0$, for $\beta_{m0} = \beta_{m0}\, a_{00} = \delta_{m0} = 0$. Hence by induction

$$\beta_{mn} = 0, \qquad (n < m) \tag{2, 2}$$

Case 2. $n = m$: $(\delta_{nn} = 1)$.

$$\beta_{nn} = \beta_{nn}\, a_{nn} = \sum_{r=0}^{n} \beta_{nr}\, a_{rn} = \delta_{nn}$$

$$i.e., \quad \beta_{nn} = 1 \tag{2, 3}$$

Case 3. $n > m$: $(\delta_{mn} = 0)$. Let $n = m + \rho$, then

$$\sum_{r=0}^{n} \beta_{mr}\, a_{rn} = \sum_{r=m}^{r=n} \beta_{mr}\, a_{rn}$$

$$= \sum_{k=0}^{\rho} \beta_{m,m+k}\, a_{m+k,m+\rho}$$

$$= \beta_{m,m+\rho} + \sum_{k=0}^{\rho-1} a_{m+k,m+\rho}\, \beta_{m,m+k}$$

$$= \beta_{m,m+\rho} - \sum_{k=0}^{\rho-1} a_{m+k,m+\rho}\, \beta_{m,m+k}$$

and $\sum_{r=0}^{n} \beta_{mr}\, a_{rn} = \delta_{mn} = \delta_{m,m+\rho} = 0$, *i.e.*

$$\beta_{m,m+\rho} - \sum_{k=0}^{\rho-1} a_{m+k,m+\rho}\, \beta_{m,m+k} = 0 \tag{2, 4}$$

Solving for $\beta_{m,m+\rho}$ from the set of equations (2, 4) we get at once

$$\beta_{mm} = 1, \quad \beta_{m,m+1} = a_{m,m+1}$$

$$\beta_{m,m+\rho} = \begin{vmatrix} a_{m,m+\rho} & \cdots & \cdots & a_{m,m+\rho} \\ -1 & a_{m+1,m+2} & \cdots & a_{m+1,m+\rho} \\ 0 & -1 & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ 0 & \cdot & -1 & a_{m+\rho-1,m+\rho} \end{vmatrix} \tag{2, 5}$$

Expanding the determinant in terms of the first row, we get

$$\beta_{m,\,m+\rho} - \sum_{k=1}^{\rho} a_{m,\,m+k}\,\beta_{m+k,\,m+\rho} = 0 \qquad (2,\,6)$$

which proves that

$$A \cdot B = \| \delta_{mn} \| = B.A.$$

We denote the transformation corresponding to B as T^{-1} where A defines T.

§ 3. *Illustrative Theorems.*

We give three theorems which, although quite obvious, are noted here for the sake of completeness of the exposition of the structure of the algebra of the transformations (T).

THEOREM 1: *If* $\{x_n\}$ *be a* $\left[\frac{\text{bounded}}{\text{null}}\right]$ *sequence, then* $y_n = T(x_n)$ *is*

$$a \left[\frac{\text{bounded}}{\text{null}}\right] \text{ sequence.}$$

Let $\bar{x}_{n_0}$ be the upper bound of $|x_n|$ for $n \geqslant n_0$, then

$$|y_n| = |T(x_n)| = \left| \sum_{\rho=0}^{\infty} a_{n,\,n+\rho}\, x_{n+\rho} \right|$$

$$\leqslant \bar{x}_n \left\{ 1 - \sum_{\rho=1}^{\infty} a_{n,\,n+\rho} \right\}$$

$$< 2\bar{x}_n, \text{ using } (d) \text{ of } (2,\,1). \qquad (3,\,1)$$

Hence the theorem is proved. Denoting the matrices corresponding to T_1, T_2, and (T_1, T_2) by A_1, A_2, and $A_1 \cdot A_2$ respectively, we have

THEOREM 2: *If* $\{x_n\}$ *be a* $\left[\frac{\text{bounded}}{\text{null}}\right]$ *sequence then* $(T_1\,T_2)\,(x_n)$, *and* $(T_2\,T_1)$ (x_n) *are* $\left[\frac{\text{bounded}}{\text{null}}\right]$ *sequences, and* $(T_1\,T_2)\,(x_n) = T_1\,[T_2\,(x_n)]$.

In general $(T_1\,T_2) \neq (T_2\,T_1)$.

Let $A_1 = \| a_{mn} \|$, $A_2 = \| \beta_{mn} \|$. If ${}_1A_1\,A_2 = \| C_{mn} \|$

$$C_{mn} = \Sigma a_{mj}\,\beta_{jn} = 0, \quad \text{if } n < m$$

$$= 1, \quad \text{if } m = n, \text{ and}$$

$$C_{n,\,n+\rho} = \sum_{r=0}^{\rho} a_{n,\,n+r}\;\beta_{n+r,\,n+\rho}.$$

$$|C_{n,\,n+\rho}| \leqslant \sum_{0}^{\rho} |a_{n,\,n+r}|\;|\beta_{n+r,\,n+\rho}|.$$

Now $$|(T_1\,T_2)\,(x_n)| \leqslant \sum_{\rho=0}^{\infty} |C_{n,\,n+\rho}|\,|x_{n+\rho}|$$

$$\leqslant \bar{x}_{n_0} \cdot \sum_{\rho=0}^{\infty} \cdot \sum_{r=0}^{\rho} |a_{n,\,n+r}| \cdot |\beta_{n+r,\,n+\rho}|$$

$$\leqslant \bar{x}_{n_0} \cdot \sum_{r=0}^{\infty} |a_{n,\,n+r}| \cdot \sum_{\rho=r}^{\infty} |\beta_{n+r,\,n+\rho}|.$$

Since $\sum_{r=0}^{\infty} |a_{n,\,n+r}| \leqslant 2$, $\sum_{r=0}^{\infty} |\beta_{n,\,n+r}| \leqslant 2$

$$|(T_1\,T_2)\,(x_n)| \leqslant 4\bar{x}_{n_0}, \tag{3, 2}$$

which proves the first portion of the theorem. Again,

$$T_1\,[T_2\,(x_n)] = \sum_{r=0}^{\infty} a_{n,\,n+r} \sum_{\rho=r}^{\infty} \beta_{n+r,\,n+\rho}\,x_{n+\rho}$$

$$= \sum_{\rho=0}^{\infty} \left(\sum_{r=0}^{\rho} a_{n,\,n+r}\,\beta_{n+r,\,n+\rho} \right) \cdot x_{n+\rho},$$

since the latter series is absolutely convergent. Therefore,

$$T_1\,[T_2\,(x_n)] = \sum_{\rho=0}^{\infty} c_{n,\,n+\rho}\,x_{n+\rho} = (T_1\,T_2)\,(x_{n+\rho}).$$

This could be easily generalised to the product of any finite number of transformations. Also since the multiple series concerned are all absolutely convergent, we have

THEOREM 3: $T_1\,\{T_2\,[T_3\,(x)]\} = (T_1\,T_2)\,[T_3\,(x)] = T_1\,[(T_2\,T_3)\,(x)] = (T_1\,T_2\,T_3)\,(x)$, *where* $(T_1\,T_2\,T_3)$ *is defined by* $A_1 \cdot A_2 \cdot A_3$. (Proof being very similar to that of Theorem II).

Both the theorems 2 and 3 could be generalised to a finite number of T's. Since in general $\Sigma\ a_{n,\,n+r} \cdot \beta_{n+r,\,n+\rho} \neq \Sigma\ \beta_{n,\,n+r} \cdot a_{n+r,\,n+\rho}$ we have $(T_1\,T_2) \neq (T_2\,T_1)$. But if all the terms in any line parallel to the diagonal of A_1 have the same value; *i.e.*,

$$\left.\begin{aligned} a_{01} &= a_{12} = \cdots = a_{n,\,n+1} = \cdots, \\ a_{02} &= a_{13} = \cdots = a_{n,\,n+2} = \cdots, \end{aligned}\right\} \tag{3, 3}$$

and a similar condition holds for A_2, then $(T_1\,T_2) = (T_2\,T_1)$.

§ 4. *Preliminary Lemmas.*

Before we proceed to Theorem 4 about the existence of a unique reciprocal, we shall prove here a set of lemmas to be used later on.

Let T_0 correspond to $\|a_{mn}\|$. By definition $a_{nn} = 1$.

We will define $-a_{mn} = a_{mn}$, so that $a_{mn} \geqslant 0$, for $n \geqslant m + 1$.

We shall prove later, in § 5, that $\| \beta_{mn} \|$ defines T_0^{-1}. For the present we shall collect together the following characterisations of the elements of $\| \beta_{mn} \|$.

By (2·2) $\beta_{mn} = 0 \ (n < m)$ (4, 1)

By (2·3) $\beta_{nn} = 1.$ (4, 2)

Since all the $\alpha_{n,\, n+\rho}$ are $\geqslant 0$, we have

$$\beta_{n,\, n+\rho} \geqslant 0 \ (\rho \geqslant 0) \ \text{ by (2·5).} \tag{4, 3}$$

Let us assume $\beta_{n,\, n+\rho} \leqslant 1$ for all n and $\rho = 0, 1, 2, \cdots \rho_0$. Then by (2, 6)

$$\beta_{n,\, n+\rho_0+1} = \sum_{r=1}^{r=1+\rho_0} \alpha_{n,\, n+r}\, \beta_{n+r,\, n+\rho_0+1} \leqslant \sum_{r=1}^{1+\rho_0} \alpha_{n,\, n+r} \leqslant 1.$$

Hence by induction for all n and all ρ, $\beta_{n,\, n+\rho} \leqslant 1$, since for $\rho = 0$ $\beta_{nn} = 1$. (4, 4)

Let $\| \beta^1_{mn} \|$ and $\| \beta^2_{mn} \|$ correspond to T_1^{-1} and T_2^{-1}; then we define the transformation $(T_1^{-1} T_2^{-1})$ by

$$\| \beta^1_{mn} \| \cdot \| \beta^2_{mn} \| = \| \bar{\beta}_{mn} \| \tag{4, 5}$$

Since $\bar{\beta}_{mn} = \sum_j \beta^1_{mj} \cdot \beta^2_{jn}$, properties (4, 1) – (4,3) also hold good for $\bar{\beta}_{mn}$.

Corresponding to (4, 4) we have

$$\bar{\beta}_{n,\, n+\rho} = \sum_{r=0}^{\rho} \beta^1_{n,\, n+r}\, \beta^2_{n+r,\, n+\rho}$$

$$\bar{\beta}_{n,\, n+\rho} \leqslant (\rho + 1) \tag{4, 5a}$$

If $\| \bar{\beta}_{mn} \|$ corresponds to the product of k such transformations

$$\text{then} \quad \bar{\beta}_{n,\, n+\rho} \leqslant (\rho + 1)^{k-1}. \tag{4, 5b}$$

Writing the system of equations (2, 4) at length, we have

$$\left.\begin{aligned}
&\beta_{nn} = 1 \\
&\beta_{n,\, n+1} = \alpha_{n,\, n+1}\, \beta_{nn} \\
&\beta_{n,\, n+2} = \beta_{nn}\, \alpha_{n,\, n+2} + \beta_{n,\, n+1}\, \alpha_{n+1,\, n+2} \\
&\cdots\cdots\cdots\cdots\cdots\cdots \\
&\beta_{n,\, n+\rho} = \beta_{nn}\, \alpha_{n,\, n+\rho} + \beta_{n,\, n+1}\, \alpha_{n+1,\, n+\rho} + \cdots + \beta_{n,\, n+\rho-1}\, \alpha_{n+\rho-1,\, n+\rho}
\end{aligned}\right\}$$

Adding we get

$$\beta_{nn} \left(1 - \sum_{r=1}^{\rho} \alpha_{n,\, n+r}\right) + \beta_{n,\, n+1} \left(1 - \sum_{r=2}^{\rho} \alpha_{n+1,\, n+r}\right) + \cdots + \beta_{n,\, n+\rho}\,(1) = 1. \tag{4, 6}$$

Let $\quad R_{n,\, n+\rho} = 1 - \sum_{r=1}^{\rho} \alpha_{n,\, n+r}, \quad (\text{for } \rho > 1) \text{ and } R_{n,\, n} = 1.$

Then (4, 6) can be written as

$$\sum_{r=0}^{\rho} \beta_{n,\,n+r}\, R_{n+r,\,n+\rho} = 1. \qquad (4,\ 6a)$$

It is to be noted that $R_{n,\,n+\rho} \geqslant 0$ since by (d) of $2\cdot1$ $\sum_{1}^{\infty} a_{n,\,n+r} \leqslant 1$.

If in condition (d) of $(2\cdot1)$ we have $\sum_{\rho=1}^{\infty} a_{n,\,n+\rho} \leqslant k < 1$, for all n, then from (4, 6) we get

$$\sum_{r=0}^{\rho} \beta_{n,\,n+r}\, R_{n+r,\,n+\rho} = 1,$$

and $$R_{n,n+\rho} = 1 - \sum_{r=1}^{\rho} a_{n,\,n+r} \geqslant 1 - k\,;$$

hence $$(1-k) \sum_{r=0}^{\rho} \beta_{n,\,n+r} \leqslant 1.$$

Hence $$\sum_{r=0}^{\infty} \beta_{n,\,n+r} \leqslant \frac{1}{1-k}. \qquad (4,\ 7)$$

Again if in condition (d) of $(2\cdot1)$

Let $\sum_{r=1}^{\infty} a_{n,\,n+r} = 1$, for all n, then it can be shown that

$$\sum_{r=0}^{\infty} \beta_{n,\,n+r} \text{ diverges.} \qquad (4,\ 8)$$

Suppose that it converges; then choose k such that $\sum_{n=k}^{\infty} \beta_{n,\,n+\rho} \leqslant \epsilon$.

$$\sum_{n=0}^{\rho} \beta_{n,\,n+r}\, R_{n+r,\,n+\rho} = \sum_{r=0}^{k-1} + \sum_{r=k}^{\rho} = A + B\,;$$

$B < \sum_{k}^{\infty} \beta_{n,\,n+r}$, since $R_{n,\,n+\rho} \leqslant 1$ for all n and ρ; since by hypothesis $\sum_{0}^{\infty} a_{n,\,n+r} = 1$, $R_{n,\,n+\rho} \to 0$ as $p \to \infty$ (for every n). Now, $A < \sum_{r=0}^{k-1} R_{n+r,\,n+\rho}$. Choosing ρ sufficiently large

such that $R_{n+r,\,n+\rho} \leqslant \frac{\epsilon}{k}$, for $r = 0, 1, \cdots, k-1$.

$$A \leqslant \epsilon, \text{ for } \rho \geqslant \rho_0.$$

Hence, $\Sigma\, \beta_{n,\,n+r}\, R_{n+r,\,n+\rho} \leqslant 2\epsilon$ which contradicts $4\cdot6$

Hence, $\sum_{\rho=0}^{\infty} \beta_{n,\,n+\rho}$ diverges. (4, 8)

§ 5. *Theorem of Unique Reciprocal Transformation for Null Sequences.*

We will now show that every transformation (T_0) has a unique reciprocal (T_0^{-1}) given by $\| \beta_{mn} \|$ [as defined in (4,1)], when applied to null sequences, *i.e.*,

THEOREM 4: *If* $\{x_n\}$ *be a null sequence, and* $y_n = T_0(x_n) = \sum_{\rho=0}^{\infty} a_{n,n+\rho} x_{n+\rho}$, *then* $x_n = T_0^{-1}(y_n) = \sum_{r=0}^{\infty} \beta_{n,n+r} y_{n+r}$, *and if the sequence* $\{y_n\}$ *be given, under the restriction that* $\{x_n\}$ *be a null sequence, the infinite set of equations* $\sum_{\rho=0}^{\infty} a_{n,n+\rho} x_{n+\rho} = y_n$, $(n = 0, 1, \cdots)$ *has utmost one solution.*

Proof:—Defining $\alpha_{m,n}$ as in § 4,

$$T_0(x_n) = x_n - \sum_{1}^{\infty} a_{n,n+r} x_{n+r} = y_n. \tag{5, 1}$$

Let $\bar{x}_{n_0}$ be the upper bound of $|x_n|$ for all $n \geqslant n_0$, and let

$$\gamma_{n,n+\rho} = \sum_{r=\rho+1}^{\infty} a_{n,n+r}. \tag{5, 2}$$

Then,

$$\left.\begin{aligned} &T_0(x_n) = x_n - \sum_{1}^{\rho} a_{n,n+r} x_{n+r} + \theta_{,}\gamma_{n,n+\rho}\,\bar{x}_{n+\rho} = y_n. \\ &\text{Similarly} \\ &T_0(x_{n+k}) = x_{n+k} - \sum_{k+1}^{\rho} a_{n,n+r} x_{n+r} + \theta_k \cdot \gamma_{n+k,n+\rho}\,\bar{x}_{n+\rho} = y_{n+k} \end{aligned}\right\}$$

for $k = 0, 1, \cdots \rho$ with $-1 \leqslant \theta_k \leqslant 1$.

$$\begin{aligned} \text{The sum } \sum_{r=0}^{\rho} \beta_{n,n+r} T_0(x_{n+r}) &= \Sigma\, \beta_{n,n+r} \Big(x_{n+r} - \sum_{k=r+1}^{\rho} a_{n,n+k} x_{n+k}\Big) \\ &\quad + \Big(\Sigma\, \theta_k \cdot \beta_{n,n+k} \gamma_{n+k,n+\rho}\Big)\,\bar{x}_{n+\rho} \\ &= A + B\,\bar{x}_{n+\rho} = \sum_{r=0}^{\rho} \beta_{n,n+r} y_{n+r}. \end{aligned} \tag{5,3}$$

$$\begin{aligned} \text{Now,} \qquad A &= \beta_{nn} x_n + \sum_{r=1}^{\rho} x_{n+r} \Big(\beta_{n,n+r} - \sum_{k=0}^{r-1} \beta_{n,n+k}\, a_{n+k,n+r}\Big) \\ &= x_n, \text{ by (2, 4).} \end{aligned}$$

$$|B| < \sum_{k=0}^{\rho} \beta_{n,n+k} \gamma_{n+k,n+\rho} \tag{5, 4}$$

From condition (d) of 2·1 and 5·2 we have

$$\gamma_{n,n+\rho} = \sum_{r=1}^{\infty} a_{n,n+r} - \sum_{r=1}^{\rho} a_{n,n+r} \leqslant 1 - \sum_{r=1}^{\rho}.$$

Hence $\gamma_{n,\,n+\rho} \leqslant R_{n,\,n+\rho}$ for all n and $\rho > 0$. Therefore using (4, 6*a*) we derive from (5, 4) that

$\sum_{k=0}^{\rho} \beta_{n,\,n+k}\,\gamma_{n+k,\,n+\rho} \leqslant 1$ and $|B| < 1$. Thus (5, 3) gives

$$x_n + \theta\,\bar{x}_{n+\rho} = \sum_{0}^{\rho} \beta_{n,\,n+r}\,y_{n+r} \qquad (-1 \leqslant \theta \leqslant 1). \tag{5, 5}$$

Since $\{x_n\}$ is a null sequence, $x_{n+\rho} \to 0$ as $\rho \to \infty$; therefore

$$x_n = \sum_{r=0}^{\infty} \beta_{n,\,n+r}\,y_{n+r} \tag{5, 6}$$

$$i.e., \quad x_n = T_0^{-1}(y_n) = T_0^{-1}\,T_0\,(x_n).$$

To prove the uniqueness of the solution when it exists under the condition that $\{x_n\}$ be a null sequence, we proceed as follows :—

Let $\{x_n^1\}$ and $\{x_n^2\}$ be two null sequences which are solutions of the set of equations

$$x_n - \sum_{r=1}^{\infty} a_{n,n+r}\,x_{n+r} = y_n, \qquad (n = 0, 1, \cdots)$$

y_n being given. Let $Z_n = x_n^1 - x_n^2$, then by hypothesis, $\{z_n\}$ is a null sequence, and

$$z_n - \sum_{r=1}^{\infty} a_{n,n+r}\,z_{n+r} = 0.$$

Applying the result (5, 5), we have

$$z_n + \theta\,z_{n+\rho} = 0, \quad \text{where } -1 \leqslant \theta \leqslant 1.$$

Therefore $z_n \equiv 0$, and hence the uniqueness of the solution.

Note.—(1) Let us take a (T) for which

$$\sum_{r=1}^{\infty} a_{n,\,n+r} = 1\ ; \quad (\text{for all } n).$$

Then if $\{x_n\}$ be a solution of $T(x_n) = y_n$, so is the sequence $\{L + x_n\}$ also a solution, for if L be a constant $T(L) = 0$. This shows the need for restricting $\{x_n\}$ to be a null sequence for the existence of a unique solution.

(2) For the same (T) as in note (1) it follows, by using (4, 8), that $\sum_{0}^{\infty} \beta_{n,\,n+r}$ diverges. We can find a null sequence $\{y_n\}$ such that $\Sigma\,\beta_{n_0,\,n_0+r}\,y_{n_0+r}$ diverges for one particular value n_0. Hence $T^{-1}(y_n)$ will, in general, have no meaning.

§ 6. *Complement to Theorem 4 and a Corollary.*

The question raised by the note in § 5 leads us to examine the necessary and sufficient conditions that the sequence $\{y_n\}$ must satisfy in order that the

set of equations in x

$$T(x_n) = y_n$$

has one solution $\{x_n\}$ which is a null sequence. We shall now prove

The sole condition (C) *is that the set of series* $\sum^{\infty} \beta_{mn} y_n$ *be* uniformly convergent *with regard to* m *for all* $m \geqslant 0$.

(a) *Proof that* (C) *is necessary:* Suppose that $\{x_n\}$ a null sequence is a solution of the set of equations $T(x_n) = y_n$. Then from (5, 5) — (5, 6)

$$x_m + \theta \bar{x}_A = \sum_{n=0}^{A} \beta_{mn} y_n$$

$$= \sum^{\infty} - \sum_{n=A+1}^{\infty} \qquad \text{for all } m \leqslant A$$

$$= x_m - \sum_{n=A+1}^{\infty}$$

$$\therefore \sum_{A+1}^{\infty} \beta_{m,n} y_n = \theta \bar{x}_A \qquad -1 \leqslant \theta \leqslant 1$$

(For all $m \geqslant A + 1$).

$$\sum_{A+1}^{\infty} \beta_{mn} y_n = \sum_{0}^{\infty} \beta_{mn} y_n = x_m, \text{ since } \beta_{mn} = 0 \text{ for } n < m.$$

Therefore,

$$\left| \sum_{n=A+1}^{\infty} \beta_{mn} y_n \right| \leqslant \bar{x}_A, \qquad \text{for all } m \geqslant 0$$

and

$$\left| \sum_{n=n_0}^{\infty} \beta_{mn} y_n \right| \leqslant x_{n_0} \leqslant \bar{x}_A, \quad \text{for all } n_0 \geqslant A,$$

since $\bar{x}_{n_0}$, being the upper bound of x_n for $n \geqslant n_0$, is easily seen to be a monotonic sequence tending to zero.

Hence the condition (C) is necessary.

(b) *To prove that* (C) *is sufficient*: Let $\epsilon > 0$, and A_0 be so chosen that for all $A \geqslant A_0$, we have

$$\left| \sum_{A+1}^{\infty} \beta_{mn} y_n \right| \leqslant \epsilon. \qquad (6, 1)$$

Let x_n be defined by

$$x_n = \sum_{\rho=0}^{\infty} \beta_{n\rho} y_\rho$$

when $n < A$, $\quad x_n = \overset{\rho=A}{\Sigma} \beta_{n\rho} y_\rho + \overset{\infty}{\underset{A+1}{\Sigma}}$

$$= \overset{\rho=A}{\Sigma} + \theta\epsilon$$

$$x_{n+r} = \overset{\rho=A}{\Sigma} \beta_{n+r,\rho} y_\rho + \theta_r \epsilon, \qquad n + r \leqslant A$$

and, $\quad x_{A+k} = \overset{\rho=A}{\Sigma} \beta_{A+k,\rho} y_\rho + \overset{\infty}{\underset{A+1}{\Sigma}}$

$$= \overset{\infty}{\underset{A+1}{\Sigma}} = \theta_{A+k} \cdot \epsilon, \quad \text{since } \beta_{mn} = 0 \quad (n<m).$$

Therefore, $x_n - \overset{A}{\underset{\rho=n+1}{\Sigma}} \alpha_{n\rho} x_\rho = \overset{A}{\underset{\rho=n}{\Sigma}} \beta_{n\rho} y_\rho - \overset{A}{\underset{m=n+1}{\Sigma}} \alpha_{nm} \cdot \overset{A}{\Sigma} \beta_{m\rho} y_\rho$

$$+ \text{a remainder (R).} \qquad (6, 2)$$

Also, $\quad |R| < \epsilon + \overset{A}{\underset{\rho=n+1}{\Sigma}} \alpha_{n\rho}\, \epsilon \leqslant 2\epsilon. \quad \text{since} \overset{\infty}{\underset{n+1}{\Sigma}} \alpha_{n,\rho} \leqslant 1.$

The first two terms on the right-hand side of (6, 2)

$$= \beta_{nn} y_n + \overset{A}{\underset{\rho=n+1}{\Sigma}} (\beta_{n\rho} - \Sigma \alpha_{nm} \beta_{m\rho}) y_\rho$$

$$= y_n. \qquad \text{by } 2\cdot 6$$

Hence, $x_n - \overset{A}{\underset{n+1}{\Sigma}} \alpha_{n\rho} x_\rho = y_n + 2\theta\epsilon$, and since

$$|x_{A+k}| \leqslant \epsilon, \text{ for all } k \geqslant 1$$

$$\left| \overset{\infty}{\underset{\rho=A+1}{\Sigma}} \alpha_{n\rho} x_\rho \right| \leqslant \epsilon \overset{\infty}{\underset{A+1}{\Sigma}} \alpha_{n\rho} \leqslant \epsilon. \quad \text{Therefore}$$

$$x_n - \overset{\infty}{\underset{\rho=n+1}{\Sigma}} \alpha_{n\rho} x_\rho = y_n + 2\theta\epsilon - \overset{\infty}{\underset{\rho=A+1}{\Sigma}} \alpha_{n\rho} x_\rho = y_n + 3\theta'\epsilon$$

i.e., $|T(x_n) - y_n| \leqslant 3\epsilon$.

Since ϵ is arbitrary, and also $|x_{A+k}| \leqslant \epsilon$, $x_n \to 0$ as $n \to \infty$, we have $T(x_n) = y_n$ which proves that (C) is sufficient. We may thus enunciate the THEOREM: *Under Condition* (C)

$$T_1 [T_1^{-1} (y_n)] = y_n. \qquad (6, 3)$$

Cor. 1 :—*If* $\{x_n\}$ *be a null sequence, and* $(T_1 T_2)(x_n) = y_n$ then

$$x_n = \Sigma \beta^2_{n,\rho} \cdot \Sigma \beta^1_{\rho,r} \cdot y_r$$

where $\| \beta_{mn}{}^1 \|$ *defines* T_1^{-1} *and* $\| \beta_{mn}{}^2 \|$ *defines* T_2^{-1} as in (4, 5).

Proof:—Let $T_2(x_n) = z_n$, then $T_1(z_n) = y_n$. Since $\{x_n\}$ is a null sequence, it follows from Theorem 1 that $\{z_n\}$ is also a null sequence. Hence

$$z_n = \Sigma\, \beta^1{}_{n\rho}\, y_\rho$$

and $$x_n = \Sigma\, \beta^2{}_{n,\rho}\, z_\rho = \Sigma\, \beta^2{}_{n\rho} \cdot \Sigma\, \beta^1{}_{\rho r}\, y_r \text{ by Theorem IV}$$

or $$x_n = T_2^{-1}[T_1^{-1}(y_n)].$$

In general

$$\Sigma\, \beta_{n\rho}{}^2 \cdot \Sigma\, \beta_{\rho r}{}^1\, y_r \neq \Sigma\, \bar{\beta}_{n\rho}\, y_\rho \quad \text{with } \|\bar{\beta}_{mn}\| \text{ defined as in (4, 5),}$$

except under special conditions, *i.e.*, in general

$$T_1^{-1}(T_1^{-1}) \neq (T_2^{-1}\, T_1^{-1}).$$

We shall discuss in Part II the set of conditions under which the equality can be true, as well as other related questions as to the validity of several types of combinations of the transformations.

KINETICS OF THE REACTION BETWEEN BENZYL CHLORIDE AND FORMIC ACID.

By L. S. Heble and T. S. Wheeler.

(From the Royal Institute of Science, Bombay.)

Received May 18, 1938.

Gavankar, Heble and Wheeler[1] have shown that ω-halogenated toluenes react with formic acid to give hydrogen halide, carbon monoxide and the corresponding ω-hydroxylated toluenes or the derivatives formed by loss of water. Thus benzal chloride and benzotrichloride give, respectively benzaldehyde and benzoic acid. Benzyl chloride and bromide also react though more slowly with evolution of hydrogen halide and carbon monoxide; here benzyl alcohol has not been isolated, possibly because it reacts with the formic acid. The last reaction can be written:

$$C_6H_5CH_2Cl + HCOOH = C_6H_5CH_2OH + HCl + CO.$$

Based on this work, a method has been evolved for the estimation of side-chain halogen in simple aromatic compounds (Gavankar *et al.*, *loc. cit.*).

The present paper describes a study of the kinetics of the reaction between formic acid and benzyl chloride. The conditions differ from those of the majority of reactions previously investigated in that there is no solvent or diluent in the system. Not much is known regarding the kinetics of such highly condensed systems* so that the interpretation of the results is difficult. However, as is shown below, the application of a theory of reactions in liquids discussed by one of us[2] indicates the presence in formic acid of a small proportion of a reactive form of the acid such as has been postulated previously by Seshadri.[3]

Experimental.

An accurately measured quantity of anhydrous formic acid (Kahlbaum) was introduced into a glass-stoppered reaction vessel of the gas wash-bottle type fitted with two delivery tubes, one cut short and the other extending to the bottom of the vessel. The longer tube served to admit nitrogen,

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[1] *J. Univ. Bombay*, 1937, 6(2), 112.

* For previous work on the subject from this laboratory see *J. Phys. Chem.*, 1935, 39, 727, 901, 907; *Proc. Ind. Acad. Sci.*, 1935, 2, 265, 483, 605; 1936, 4, 91.

[2] *Proc. Ind. Acad. Sci.*, 1936, 4, 291.

[3] *Curr. Sci.*, 1936, 4, 650.

while the shorter tube could be connected by means of a T-tap to either of two wash-bottles containing aqueous silver nitrate solution. The reaction vessel was heated in a water thermostat, controlled to within 0·5°, and when it had attained the required temperature, the requisite quantity of benzyl chloride (Kahlbaum's " Purest ") was introduced, and a current of nitrogen (two bubbles per second) freed from oxygen (alkaline pyrogallol) and dried (sulphuric acid) was led through the liquid. Initial experiments showed that this rate removed all of the hydrogen chloride, and that there was no appreciable loss of formic acid from the reaction vessel. The hydrogen chloride evolved was absorbed by the aqueous silver nitrate; at the end of a stated time the gas current was switched by means of the T-tap into the other wash-bottle, and the first replaced by one containing a fresh solution of silver nitrate. The alternate use of two wash-bottles was continued until the run was complete. The precipitated silver halide was collected and weighed in a gooch crucible.

Experimental Results.

Experiments were made at 80°, 90° and 100° with various concentrations of the halide in formic acid. The quantity of the reacting liquid used was also varied to eliminate the possibility of systematic errors; for example, if an appreciable quantity of hydrogen chloride was retained on the sides of the vessel above the liquid then the effect of this error would be reduced with increase in the volume of reacting liquid, and the results obtained with say 5 c.c. of formic acid and 0·1 c.c. benzyl chloride would not agree with those obtained with double the quantitites.

Actually no such disagreement was obtained. As the acid was always in large excess, the reaction would be expected to be unimolecular, and as will be seen from Table I a moderately good constant was obtained. In illustration of the type of experimental results the following figures may be quoted:—

Temp. 80°. 0·5 *c.c. of benzyl chloride in* 5 *c.c. of formic acid.*

(See Table I, serial No. 5.)

Times in minutes ..	30	40	60	80	90	120	180
% Conversion of benzyl chloride ..	8·9	12·7	18·0	23·0	24·7	32·5	41·4
K (reciprocal mins.; logs to base 10) $\times 10^4$ ..	14	15	14	14	14	14	13

Temp. 90°. 2·0 *c.c. of benzyl chloride in* 10 *c.c. of formic acid.*
(See Table I, serial No. 13.)

Time in minutes ..	20	40	60	80	100
% Conversion of benzyl chloride ..	8·0	15·5	21·8	27·1	32·8
K (reciprocal mins. ; logs to base 10) $\times 10^4$	18	18	18	17	17

Table I summarises all the values of K obtained. These values fall as the concentration of benzyl chloride increases, and it is found that plot of the concentration against the values of K gives approximately a straight line for each temperature.

Reactions are known in which the velocity increases with dilution ; for example, the velocity of decarboxylation of trichloro-acetic acid in water.[4] Many suggestions have been made to account for this phenomena, but the cause is as yet not definitely known. A possible explanation for the reaction under examination will be discussed below.

Values for the Arrhenius critical increment (E) have been calculated in the usual manner by plotting log K against $\frac{1}{T}$, and measuring the slope of the approximately straight line thus obtained. The values of E increase with increase in concentration ; this is to some extent a corollary to the fall in the reaction velocity.

Calculation of the value of K from the observed value of E.—In a paper on the theoretical aspect of reactions in liquids[5] it has been shown that K for a unimolecular reaction undergone by a solute in the liquid phase is given by

$$K = 2{\cdot}80 \times 10^{12} \frac{P^4}{V^{\frac{11}{3}} M^{\frac{1}{2}} T^{\frac{1}{2}}} e^{\frac{-E_1}{RT}} \left(\frac{E_1}{RT}\right)^{f-1} \frac{1}{\lfloor f-1}, \qquad (1)$$

where $$E_1 = E + \frac{22\,T^2\alpha}{3} + (2f-1)\,T \qquad (2)$$

P is the parachor,
V is the molecular volume,
M is the molecular weight,
α is the coefficient of cubical expansion of the solute, and
$2f$ is the number of square terms defining E_1.

In the application of equation (1) it is necessary to see if a small integral value of f can be found which will enable a value of K to be calculated in

[4] Kappanna, *Z. phys. Chem.*, (A), 1932, **158**, 355.
[5] Wheeler, *Proc. Ind. Acad. Sci.*, 1936, **4**, 291.

TABLE I.

Summary of K Values.

S. No.	Benzyl chloride initially c. c.	Formic acid initially c. c.	K (reciprocal mins.; logs to the base) 10×10^4			Mean values of K (recip. mins.; $\log_{10}$) $\times 10^4$			Corresponding values of E cals./g. mol.
			80°	90°	100°	80°	90°	100°	
1	0·1	5	17	..	48	..	..	..	..
2	,,	,,	18	33	47	..	..	..	..
3	0·2	10	17	..	48	..	..	..	..
4	,,	,,	18	36	48	18	35	48	14,200
5	0·5	5	14	26	38	..	..	..	..
6	,,	,,	,,	25	39	..	..	..	..
7	1	10	11	24	37	..	..	..	..
8	,,	,,	12	26	36	..	..	..	..
9	2	20	13	22	42	..	..	..	..
10	3	30	14	25	..	13	25	38	14,600
11	1	5	7	18	26	..	..	..	..
12	,,	,,	,,	,,	25	..	..	..	..
13	2	10	8	,,	26	..	..	..	..
14	,,	,,	7	16	27	7	18	26	17,800

agreement with the experimental value. It is found however, that even when f is put equal to one so that the calculated value of K is as small as possible, it is still many powers of 10 greater than the observed value. To illustrate the calculation :

we have for benzyl chloride at 80° :—

$$P = 283{\cdot}4\ ;\ P^4 = 6{\cdot}41 \times 10^9$$
$$V = 120\ ;\ V^{11/3} = 4{\cdot}20 \times 10^7$$
$$M = 126{\cdot}5\ ;\ M^{\frac{1}{2}} = 1{\cdot}12 \times 10$$
$$T = 353\ ;\ T^{\frac{1}{2}} = 1{\cdot}88 \times 10$$
$$a = 10^{-3}.$$

Putting $f = 1$ equation (2) gives for E_1,

$E_1 = 14{,}200 + \frac{22 \times 353^2 \times 10^{-3}}{3} + T = 15{,}500$, which on being inserted in (1) with f put equal to 1, gives,

$$K = \frac{2 \cdot 80 \times 10^{12} \times 6 \cdot 41 \times 10^9}{4 \cdot 20 \times 10^7 \times 1 \cdot 12 \times 10 \times 1 \cdot 88 \times 10} e^{\frac{-15{,}500}{2 \times 353}}$$

$$= 5 \cdot 97 \times 10^2.$$

K (observed ; reciprocal seconds ; natural logs.) $= 6 \cdot 91 \times 10^{-5}$.

Hence the calculated value of K is nearly 10^7 times greater than the observed value ; for the highest concentration examined, the ratio is of the order of 10^5. Moelwyn-Hughes[6] discusses the subject of " Slow Reactions " and cites a number of such reactions where the ratio between the calculated and observed values of K amounts to many powers of 10. He points out that any assignment of reasons for the tardiness of these reactions must be speculative, but that if one of the reagents reacts in the ionised or in a specially activated condition, then a ready explanation can be found for the results. Thus to take the reaction under discussion, if anhydrous formic acid can only react in the form : $C\begin{smallmatrix}OH\\OH\end{smallmatrix}$, assumed to be present only in traces, then the results can be satisfactorily explained. Further, if we assume that the activation of formic acid is depressed by the presence of benzyl chloride and its reaction product, then we have an explanation of the fact as the concentration of the initial benzyl chloride is increased, the velocity constant decreases.

It will be seen, therefore, that the results given above can be explained by the assumption made by Seshadri (*loc. cit.*) which was based solely on the chemical behaviour of formic acid.

Summary.

The kinetics of the reaction between benzyl chloride and anhydrous formic acid have been examined at 80, 90 and 100°. The velocity of the reaction decreases with increase in concentration of benzyl chloride in formic acid. The observed rate of the reaction is much slower than that calculated from the observed heat of activation ; a possible explanation of the tardiness of the reaction is provided by the assumption that formic acid reacts in an activated form present only in traces.

[6] *The Kinetics of Reaction in Solution*, 1933, 106.

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